ASPECTS OF SOLUTE MOVEMENT IN THE BRITISH UPLANDS

by

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ABSTRACT

The aim of this research is to determine the process by which runoff draining parts of the UK uplands becomes discoloured. Recent increases in colour are perceived as a problem due to the frequency with which EC surface water directives are breached, to the increased cost of meeting standards, to an increase in consumer complaints, and due to the possible deleterious health effects of consuming coloured potable water.

The work was conducted over the last four years, largely in the Upper Burn and Nidd valleys, north Yorkshire, and at the University of Leeds. Existing knowledge on the chemical nature and environmental genesis of coloured water is reviewed, and related to the chemical nature of coloured waters examined in this study. Analysis of water quality archives and direct monitoring of selected catchments was conducted enabling the spatial and temporal distribution of coloured waters to be determined. A tentative process theory was produced, and tested by controlled laboratory investigations.

Coloured runoff is derived from Winter Hill soil, raw acid oligo-fibrous peat, and is most intense from areas with slopes $\leq 5^{\circ}$ and high drainage densities. The seasonal pattern of colour is highly regular, and is a product of rainfall and soil moisture deficit. Colour is strongly

associated with discharge, and demonstrates the operation of a catchment flushing mechanism. Runoff is discoloured in a three phase process; colour production, solubilisation and removal. Colour is a product of organic decomposition, dependent upon microbiological activity, moisture deficit, temperature and peat structure. Solubilisation of colour is dependent upon solution pH, temperature, the chemical structure of organic molecules and the availability of iron. The removal of decomposition products, as colour, is strongly dependent on the moisture status of peat, and its ability to rewet after drying. The implications of these findings for future colour levels and for catchment and catchwater management are discussed.

"When water chokes you, what are you to drink to wash it down?" Nicomachean ethics, Aristotle (384-322 BC).

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1. AIMS AND INTRODUCTION

1.1 Aims

This research aims to identify the process by which water draining UK upland catchments becomes coloured. A two stage research method was adopted. In the first stage the distribution of coloured water was determined in both space and time. The impact of environmental influences on these distributions was determined. In the second stage, those environmental influences identified as significant to discolouration were investigated, by controlled experimentation.

The spatial distribution of colour was investigated by analyses of Water Authority archives, and by intensive sampling of several upland catchwater systems in the UK. The temporal distribution of colour was also investigated with the aid of archival data, and drew heavily on intensive field sampling of several catchments. Colour distributions were determined at a number of spatial and temporal scales.

The process of colour production and hydrologic removal was investigated by controlled laboratory experimentation. These controlled studies drew heavily on conclusions derived from the stage one analysis. Particular attention was paid to the rôle that peat, soil moisture, peat pH, and soil microbiology play in discolouration.

1.2 Introduction

The British uplands, areas over 250 m above sea level, occupy 7.3 million hectares, approximately one third of the total UK land area. They are concentrated in Scotland, Wales, northern England and the west country, and are characterised by high rainfall, low temperatures and acid soils. These conditions limit the growing season and agricultural productivity. Land use is mainly restricted to rough pasture supporting stocking densities up to 2.5 ewes ha^{-1}, improved pasture supporting 6 ewes ha^{-1} and coniferous plantation. The EC less favoured area directive (75/268/EEC) has sustained the level of improved pasture, while government policy has greatly increased the post war rate of conifer afforestation through a system of planting subsidy and tax incentive.

Due to their topography, high rainfall, remote location and low intensity land use the British uplands are well suited to the gathering and storage of water. Upland reservoirs supply approximately one third of water consumed in the UK and fulfil a vital function in river regulation. Upland water resources must therefore be considered as nationally important.

The main thrust of UK upland catchment research has until relatively recently centred on questions of quantity. Pioneer studies in Lancashire suggested that afforestation could reduce the yield of a catchment by as much as 42 % (Law, 1956). Further research, including a ten year paired

catchment study at Plynlimon, Wales, demonstrated that Laws' observations were correct and that catchment afforestation could substantially reduce water yield (eg. Rutter 1963; Calder 1976,1979; Newson 1979). These studies brought water resource agencies into direct conflict with forestry interests, dedicated to the establishment of a national timber reserve, over the strategic use of the uplands. This conflict remains to be resolved satisfactorily and the emphasis of UK upland catchment research has shifted from questions of quantity to those of quality.

Land use and climate affect the quality of upland water. Changes in these factors can produce a reduction in water quality that adversely affects potable supplies, freshwater ecosystems and the recreational value of surface waters. Potable supplies are particularly susceptible to changes in upland land use, due to the traditional method of quality protection. This consisted of catchment protection, where land use and access were strictly controlled, coupled with long storage which necessitated only simple filtration and chlorination near the point of use. However, increasing consumption has placed greater demands on upland water resources, thus reducing storage periods, while recent privatisation of the industry produces pressure to change to land uses that are not fully compatible with water gathering. These pressures greatly reduce the ability of present water treatment works to cope with deteriorations in water quality. Deteriorations in water quality can

degrade aquatic and riparian ecosystems both above, below and in impoundments. Finally, water quality reductions can reduce the amenity value of surface waters for angling and immersion sports.

This thesis examines the phenomenon of natural discoloration of water draining upland catchments. However, it should be noted that discoloration is just one of several upland water quality issues of current concern in the UK, including surface water acidification, trace metal mobilisation, catchment nutrient loss and runoff enrichment, sedimentation and deterioration in the sanitary quality of water. These issues, including discoloration, have been reviewed by Mitchell (in press). It is recognised that these upland water quality issues should not be considered in isolation from each other, and that water discoloration is only one aspect of upland water quality management, which is itself only one aspect of water resource management. Similarly, water resource management is only one of several potentially conflicting land use activities that are carried out in the British uplands.

Within the UK, the phenomenon of water discoloration was first percieved as a significant problem in Northern England, particularly in Yorkshire. Yorkshire has eighty eight direct supply reservoirs located in the headwaters of the rivers Aire, Calder, Don, Ure, Nidd and Wharfe. These reservoirs provide almost 50% of the public water supply in Yorkshire (705 Ml d^{-1} of 1373 Ml d^{-1} in 1986). About 25% of

the region's water is obtained from lowland river abstraction, much of which can be considered a secondary upland water source. The remainder comes from groundwater abstraction. The principal water supply sources and reservoir gathering grounds in Yorkshire are illustrated in figure 1.1. The gathering grounds of the upland reservoirs cover 52 300 ha, one third is owned by Yorkshire Water at present. The land use comprises Moorland (68%), Pasture and agriculture (28%) and Forestry (4%). Much of the moorland is covered by large accumulations of peat, over 6m at Ringinglow bog near Sheffield, although elsewhere the organic layer may be only a few millimetres thick. The geology of the area is largely Millstone grit with some Carboniferous limestone deposits. Water draining from both these areas tends to be very low in nutrients, but water draining limestone areas is moderately hard and slightly alkaline due to dissolved calcium carbonate. Water draining gritstone is soft and often acidic. The annual rainfall exceeds 1500 mm along the main watershed of the Pennines, and is amongst the most acidic in the country. Reliable records on rainfall pH are scarce, but the indications are that rainfall in the Yorkshire region has an average pH of 4.5 (Anon, 1987). Reservoir water is commonly soft, oligotrophic and acidic.

The water supplied from many of these reservoirs has always been coloured to a certain degree. Indeed, the removal of colour from water at treatment plants has led to complaints from some people that "all the goodness has been removed".

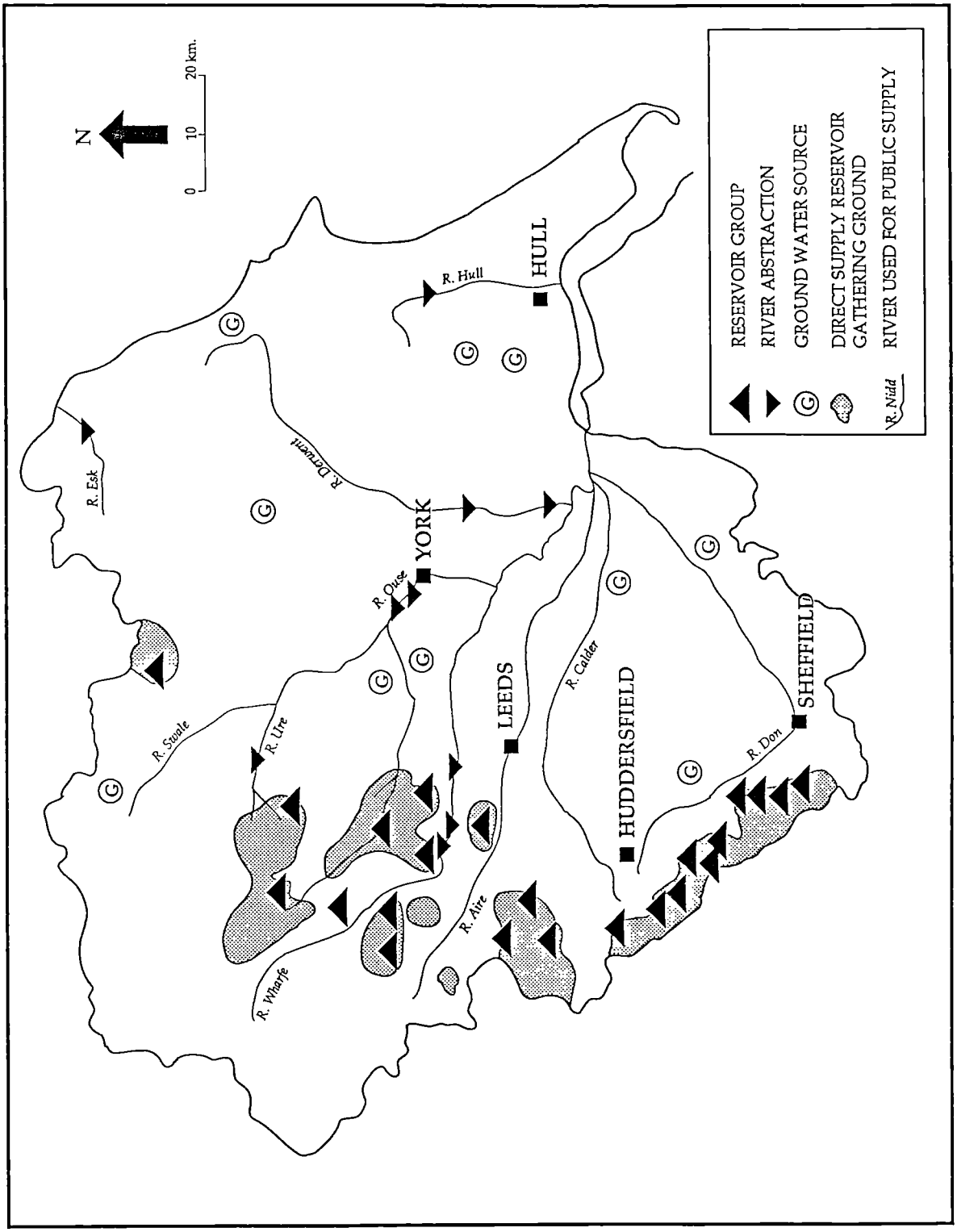


Figure 1.1 Principal Water Supply Sources in Yorkshire

This is particularly evident with consumers in remote rural areas whose water usually recieves the minimum of treatment, and is often coloured. Such people are increasingly sceptical of the benefits of being linked to a more widespread distribution network. However, most people today are used to colourless water that, for the majority of the time is supplied to their homes. Consumers have become conditioned into believing that a clear water is pure, and that conversely a coloured water is not, and is therefore undrinkable.

It is important at this stage to make a distinction between true colour, and apparent colour. Apparent colour is defined as the colour of an unfiltered water. Therefore apparent colour can include suspended solids, making a water appear more coloured than it really is. True colour is determined only after sample filtration. True colour is commonly determined after 0.45 μm membrane filtration, followed by absorbance measurement at 400 nm . This is the colour measurement technique adopted in this study. However, no standardised colour measurement method has been universally adopted, producing inconsistencies in water colour databases. Colour measurement techniques, and the difficulties associated with them are disccussed by Mitchell and McDonald (in press).

The colour of raw water from reservoirs has always exhibited a strong seasonal pattern, with minimum values in summer, & with an autumn, or early winter peak. In the autumn of 1985 record levels of colour were recorded in several

direct supply reservoirs across Yorkshire. An examination was made of water colour records for reservoirs across the region. Due to water authority reorganisation few records were available detailing water quality prior to 1974-75. However, it became clear that water colour increases were not restricted to a few isolated cases. Seasonal colour maxima were increasing markedly in many areas, and perhaps of more concern to water resource managers, there appeared to be a gradual, but consistent increase in mean annual water colour. Figure 1.2 illustrates the monthly mean colour for raw waters recieved at Thrum hall water treatment works, Yorkshire, for the period 1976-1985. Mean annual raw water colour experiences a sixfold increase, whilst the autumn maxima for the post 1976 period experiences a ten fold increase. Post 1976 colour increases have been observed at many upland water treatment works.

Other regional water utilities have also reported discoloration problems. Colour problems following the drought of 1984 have been reported by Severn-Trent, North West Water, Welsh Water and Northumbrian Water. Table 1.1 shows the post 1984 increases in raw water colour for selected reservoirs in Teeside. These water utilities were not able to identify trends in discoloration due to inadequate historic records. However, a record level of colour in 1985 was identified in a twenty year log kept by the Dumfries and Galloway water department. In addition, an upward colour trend was identified, with increases in

Figure 1.2 Raw water colour at Thrum Hall water treatment works, 1976-1985.

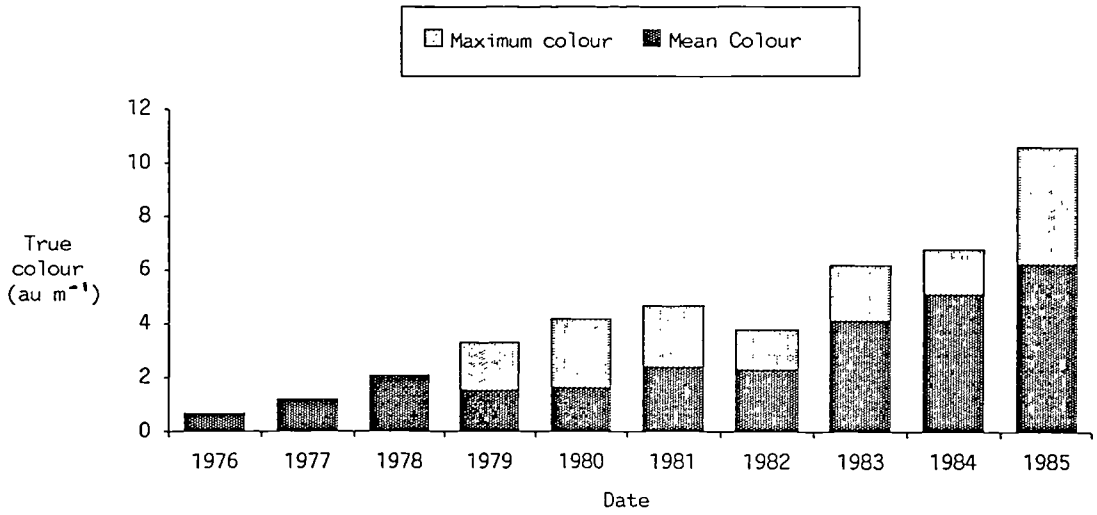
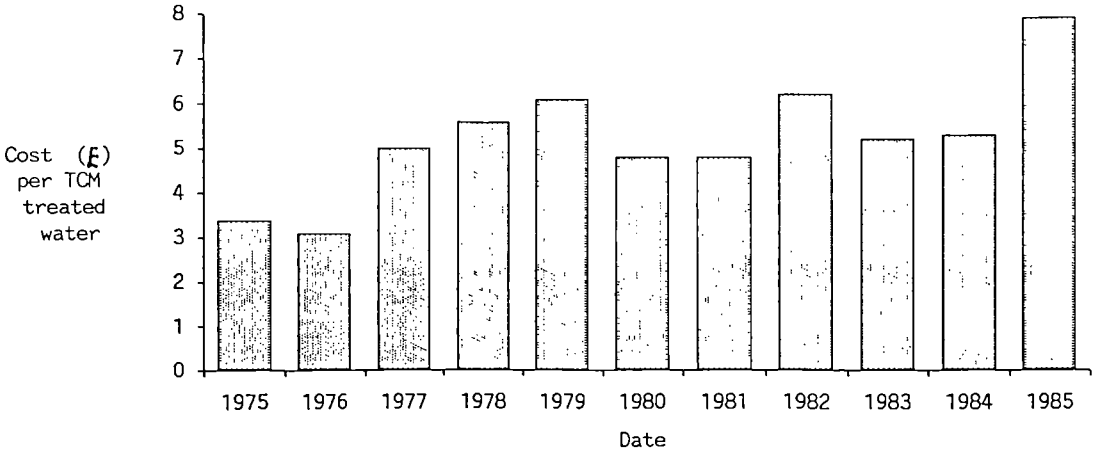


Figure 1.3 Mean annual coagulant cost at Chellow heights water treatment works, 1975-1985.



iron, manganese and acidity (Edwards et al,1988).

Table 1.1 Annual mean true raw water colours (Hazen*) for Teesdale reservoirs, Tees division, Northumbrian water. Maximum values in parenthesis.

Year	Grassholme	Balderhead	Blackton	Hury	Selset
1974-5	115(180)	110(150)	135(200)	125(200)	155(200)
1975-6	120(210)	115(135)	125(135)	110(130)	135(230)
1976-7	115(125)	115(125)	115(145)	115(125)	145(175)
1977-8	- -	- -	- -	- -	- -
1978-9	144(210)	- -	- -	128(180)	- -
1979-80	110(175)	130(150)	140(200)	125(150)	140(240)
1980-1	124(260)	120(140)	125(140)	114(150)	146(275)
1981-2	114(175)	118(130)	125(155)	- -	134(200)
1982-3	92(140)	111(150)	116(165)	101(155)	110(165)
1983-4	104(140)	111(125)	120(175)	107(130)	129(200)
1984-5	152(240)	113(136)	117(215)	123(215)	154(240)
1985-6	203(210)	168(285)	180(275)	200(260)	200(350)
1986-7	125(260)	130(140)	139(150)	125(250)	125(145)

* 1 Hazen approximates to 15 au m^{-1} @ 400 nm .

1.3 The problems arising from colour

1.3.1 Customer complaints

The EC standard for the acceptable colour of filtered drinking water is 1.5 au m^{-1} (at 400 nm). Waters that breach this standard are readily observed by the consumer,

and may give rise to complaint. In 1986, Yorkshire Water recieved 1.5 million customer complaints, of which the greatest proportion related to water colour. The pattern of consumer complaints regarding coloured water is seasonal and is broadly similar to the pattern exhibited by coloured water itself. The level of complaints is moderate throughout most of the year, but shows a marked increase during the autumn.

The long term trend of coloured water complaints is relatively constant, once the figures are adjusted for seasonal variation. However, recently there have been exceptional years when the number of consumer complaints regarding coloured water, received during the autumn period, far exceeded expectations. Table 1.2 details the number of residents in Halifax, West Yorkshire, who complained about discoloured water from 1981 to 1987. Although the data is complicated by changes in engineering works, it is apparent that the years 1981-82 and 1985-86 were exceptional in terms of consumer complaints. The population of Halifax is approximately 100 000 persons, and this data indicates that a high proportion of households are in receipt of water of an unacceptable colour. For the whole Yorkshire supply region, complaints reached a peak in the winter of 1985-86, with over 500 coloured water complaints handled each day during January 1986.

Table 1.2. Consumer complaints relating to coloured water in Halifax, West Yorkshire.

Year	Complaints
1981-2	5693
1982-3	3398
1983-4	1072
1984-5	1319
1985-6	9566 *
1986-7	933 †?

* Albert reservoir sludge filled

† last three months estimated

Market research conducted on behalf of Yorkshire Water identifies discoloured drinking water as the most serious water services problem in the region. Discoloured water accounts for half of all problems experienced by consumers, twice as many as the second most frequently experienced problem, interupted supply. When asked to rank eight water services in order of importance, the public placed the maintenance and improvement of tap water quality first. The public were asked how they viewed the change in water quality over the previous year, 1985-86. Those respondents from Leeds and Huddersfield, where the eradication of discoloured water had been made a priority, and a public information campaign had been conducted, gave the most favourable response. Clearly, the discoloration of water significantly affects the publics' perception of water utility performance.

Domestic consumers are not the only customers who find coloured waters unacceptable. Certain industrial groups are concerned about water colour, and the adverse effect it can have on the quality of the goods they produce. These groups include food processing, brewing, textiles and pulp and paper manufacture.

1.3.2 Increased operating costs

An increase in the colour of raw waters received by treatment plants results in an increase in treatment costs. These costs arise from higher chemical dose, increased filter backwashing which is expensive in terms of treated water consumption, and in higher sludge production and therefore waste disposal costs. Colour removal is achieved using a hydrolysing coagulant, typically aluminium or ferrous sulphate. Within the Yorkshire supply region, coagulant costs rose from £3.40 per TCM (1000 cubic metres) in 1975 to £5.89 per TCM in 1986. It is estimated that during the 1985-86 colour peak, where coagulant costs rose to £8.15 per TCM, an additional £57 000 was spent at one treatment plant alone, Chellow heights, supplying water to Bradford. Coagulant costs for Chellow heights, for the period 1975-86 are illustrated in figure 1.3. Other water treatment plants experienced similar increases in coagulant requirements. For example, Ramsden wood treatment works, West Yorkshire, experienced a ten fold increase from 1975-86.

Colour and the potentially toxic metal ions associated with it have different optimum pH values for their removal. The optimum pH for colour removal is 5.0-6.5, but a lower pH is required for iron coagulation. Treatment processes requiring pH values of 7.0 or above, or the temporary and localised high pH values experienced on coagulant addition, will result in the formation of metal-colour complexes which are not readily precipitated at the lower pH values required for colour removal. Therefore, successful water treatment requires more complex, multi-stage treatment. Such treatment has cost implications for the water industry.

As distribution networks become more integrated, greater use is made of upland waters. These waters are cheaper as they have lower treatment costs, and distribution is achieved by gravity, rather than pumping. However, as these upland waters become more coloured, clearer, more expensive, water may have to be pumped from river or groundwater to dilute the colour. In addition, increased use of upland waters results in reduced storage time in the reservoir. This may result in less easily treated waters arriving at water treatment works. Thus there are oportunity costs associated with the use of coloured upland waters.

1.3.3 Capital expenditure

Upland waters are a relatively cheap source of supply. Water from direct supply reservoirs are gravity fed and so have minimal pumping costs. Traditionally many of Yorkshires treatment plants were very basic, single stage filtration plants. Treatment consisted of pH correction, chlorination and limited coagulant addition. However, during colour peaks in the late 1980's, colour broke through into supply following increased coagulant addition and filter overload. Treatment efficiency at Headingley, Eccup, Langsett and Thornton Moor water works was particularly low.

The increase in incidences of colour breaking through to supply caused an acceleration and expansion in the programme to update and/or replace aged water treatment plants in the Yorkshire region. By 1995 this renewal programme will have involved a capital investment of £85 Million (at 1986 prices), equating to approximately £50 per customer. These costs include provision of new plant and the necessary pipework to redistribute supplies. Table 1.3 details projected capital expenditure for one supply region within Yorkshire by 1995 (Lucas, 1986).

Table 1.3. Projected capital expenditure to combat water discoloration for Western division by 1995.

Area	Investment programme	Cost(£M)
Kirklees	Additional treatment stage provided at Longwood and Fixby.	11.8
	Plants at Holmfirth and Homestyes are to be abandoned and be replaced by a single new plant at Holmfirth.	7.0
	Plants at Rusby Wood and Whitely abandoned and replaced by single new plant at Rusby Wood.	3.7
Calderdale	Current scheme to replace major works. Only necessary addition is extension to Todmorden plant.	1.4
Bradford	Eight plants rationalised to single extended plant at Chellow Heights. Major renewal of distribution network.	21.0
Skipton	New plant at Skipton. Plants at Keighley replaced and extended.	4.0

1.3.4 Problems with chlorination

It is well established that naturally coloured waters form Trihalomethanes (THM's) upon chlorination during water treatment (eg Meier *et al.*,1985; Hemming *et al.*,1986). THM's, such as chloroform, and other non-volatile halo-

genated compounds, by products of chlorinated coloured water, are suspected carcinogens (Lancet, 1981). The relative abundance and distribution of THM species, ranging from chloroform to bromoform, is influenced by many factors. The presence of bromide ions is the most dominant factor. Other important factors include total organic carbon concentration, pH, temperature and the presence of chlorine demanding substances such as ferrous iron and ammonia (Cooper et al, 1985). Trihalomethane concentrations for Thornton moor during the autumn of 1980 are detailed in Table 1.4. The standard pertaining at the time was 100 µg total THM.

Table 1.4 Trihalomethane concentrations ($\mu g l^{-1}$) at Thornton Moor, autumn 1980.

Date	Chloroform	Bromodichloro -methane	Bromoform	Dibromochloro -methane
8th Sep	155	8.3	0.5	0.4
17th Sep	227	14.1	0.5	0.6
25th Sep	197	10.5	0.5	0.4
1st Oct	247	12.7	0.5	0.4

The chlorination of coloured water may also cause taste and odour problems if phenols are present (Cooper et al., op. cit.). Phenols are present in colour causing organics, and their chlorination can result in the formation of distasteful chlorophenols. This problem can be avoided by the addition of Ammonia, resulting in the formation of more acceptable chloramines, which are also more effective disinfectants. However, if the correct chlorine-ammonia

ratio is not maintained, dichloramines may be formed. Dichloramines cause taste problems, and may as a by-product generate nitrites, associated with incidences of stomach cancers.

Equally effective alternatives to chlorination, such as ozonation, are available, but their possible side effects are not yet fully evaluated. Alternatives to chlorination are also likely to be more expensive.

1.3.5 Acidification

A strong positive association exists between water colour and acidity. Many of Yorkshires reservoirs are acid, pH between 4 and 5, and have been fishless throughout their life. However, in recent years there have been incidences of acid flushes, particularly in non-reservoired catchments, penetrating further downstream than ever before. In some instances these colour associated acid flushes have been the cause of fish kills, (eg. River Laver, River Skell, Lumley moor reservoir, and Gill beck, a tributary of Fewston reservoir). In October 1983 a trout farm on the River Burn suffered a mortality of 30 tonnes of Rainbow trout (Salmo irideus). The mortality was attributed to the presence of toxic metals and a pH drop of almost 4 units (Robinson, 1985).

1.3.6 Metal mobilisation

Colour is strongly correlated with pH. Highly coloured waters are very often strongly acidic, largely due to the presence of naturally occuring acids, and a scarcity of basic salts. These acidic, coloured waters are able to mobilise metal ions, such as iron, manganese and aluminium which cause their own particular problems. Iron, for instance, becomes deposited in distribution systems causing reduction in delivery capacity, and taste, odour and appearance problems when encrustations are dislodged.

Aluminium may represent a serious health problems when high concentrations are present in potable water. Aluminium absorbed into the body can cause brittle bones, anaemia and encephalopathy, a form of dementia, if absorbed in sufficient quantity. Dialysis patients and premature babies are also at risk as their kidneys are not able to remove the aluminium. Evidence from recent studies conducted in the UK, Norway, Japan and Guam (Ferry,G.,1988) suggest a strong link between high levels of aluminium in potable waters and the incidence of Alzheimers disease, a form of dementia involving irreversible damage to cortical nerve cells. Although potable waters are not the only dietary source of aluminium, high levels in water, particularly above the EC limit of 0.2 mg l^{-1}, are a source of concern to water managers.

1.3.7 Conclusion

In North and West England, in Scotland and Wales, the uplands represent the single most important source of water. Significant deterioration in the quality of this water results in breaches of EC standards, the supply of sub-standard possibly unhealthy water to consumers, and in some cases the acidification of rivers and impoundments with a consequent impact on fish populations. The publics perception of a water utilities' performance is severly affected by the discoloration of domestic water supply. These problems can be dealt with by building new treatment plants, and by uprating the performance of existing ones. However, a further means of combating the problem rests not with treatment solutions and public relations exercises, but with controlling the quality of the material that is the base product of the water industry - the raw water itself. This research aims to identify the process by which water becomes coloured, so enabling water resource and catchment managers to make informed decisions that aim to reduce the colour of water arriving at treatment plants.

2. THE NATURE OF DISCOLOURED WATER

In this chapter, consideration is given to the nature of the material that is responsible for discolouring water. In the first section a review of the literature pertaining to natural discolouration of fresh waters is presented. The complex nature and incomplete understanding of the chemical composition and structure of colour forming bodies is examined, while particular attention is paid to the rôle played by organic iron complexes. The contribution of catchment hydrological and reservoir processes to colour production is also considered.

In the second section, some analyses of locally coloured waters, collected from the principal study sites in this research, are presented. These analyses aim to demonstrate that the coloured waters studied in this thesis are broadly similar in nature to those studied in the literature review. The behaviour of coloured waters during storage and dilution, factors relevant to reservoir and catchwater management, is outlined.

2.1 The chemical composition and environmental genesis of discoloured water: literature review

2.1.1 Introduction

Fresh waters exhibiting a yellow-to-brown and even black colour are found in many parts of the world. These waters are coloured as a result of their natural environment, and should not be confused with industrial discharges of a similar colour. Such naturally coloured waters are

variously known as yellow organic, brown or black water and bog, swamp or humus water. However, these waters are most commonly referred to as discoloured or simply coloured water.

On aesthetic grounds alone coloured water is undesirable for domestic use, and accordingly the EC standard for acceptable drinking water is 1.5 au m^{-1} (at 400nm). The visual factor is not the only objection. It has been claimed that the materials responsible for colour impart taste to water, reduce chlorination efficiency, and by acting as a nutrient source encourage bacteria in the water. In addition, certain industries, in particular food processing, brewing, distilling, textiles and pulp and paper manufacture are concerned about the colour of the water they use and its possible effect on their products.

There is no evidence that coloured water is directly harmful to health. However, it is possible that through the solubilisation of trace metals, such as lead and cadmium, a coloured water could, over a long period of time, have a chronic health effect. It has been found that the chlorination of waterborne organics, such as humic and fulvic acids, is responsible for the production of mutagens (Meier et al., 1985; Hemming et al., 1986). Steelink (1977) has associated increased incidences of bladder cancer with the production of chloroform from the chlorination of humic acids.

Trihalomethane levels > 200 ug l^{-1} (EC Maximum acceptable

concentration) have been associated with high colour flows. Huck et al. (1987), found an increase in toxic or mutagenic chlorinated samples during the Canadian spring thaw when concentrations of DOC, humic acid and extractable organics was at an annual maximum. Liimatainen and Grummt (1988) found between 500 and 14 000 induced revertants per litre in chlorinated drinking water, processed from humus rich Finnish surface waters. These figures are up to twice those found elsewhere and suggest that the mammalian in vitro assays conducted by the authors are more sensitive than the salmonella (Ames) test, a view supported by Douglas et al. (1986).

2.1.2 The origins of natural colour in water

There is a general belief that colour in water is due to the presence of dissolved organic matter from natural leaching of soils and leaf litter in drainage basins. Attempts have been made to find other sources of natural colour in water. Cristafalo et al. (1962) suggest that yellow material in water results from algal excretion products. This may be true, but it is unlikely that algal metabolites contribute anything more than a very limited proportion to total discolouration. Hutchinson (1957) calculated that coloured waters had lower protein levels and higher C/N ratios than clear waters and so were unlikely to be of algal origin. Research by Shapiro (1957) and others produced similar figures for humolimnic acids extracted from coloured waters. Indeed,

there is evidence that algal populations may be responding to coloured water, not contributing to it. Shapiro (op.cit), Provasoli (1961) and Schelske (1962) all conclude that the stimulatory effect of water colour on primary productivity is due to trace metal stabilisation by humics. More specifically, colour in water could arise from the aqueous extraction of organics from living plant material, the solution of plant degradation products, the solution of soil organic matter, or a combination of these processes.

Colour is imparted to water on contact with forest debris and soil containing organic matter (Ghassemi 1963, Sylvester and Seabloom 1965). Shapiro (op.cit) using paper chromatography found similarities between the coloured water of a lake and aqueous extracts of a bottom soil, and concluded that colour did originate in soil. Christman and Ghassemi (1966) explored the possibility that colour in water is only an intermediate step in the transformation of organic matter from living or decaying woody tissue to the soil organic complex. They collected stemflow from Douglas fir during heavy rain and found it to be highly coloured, and that the colour was lost after percolating through 6in of rich organic soil. They also stated that aqueous extracts from Douglas fir bark were very 'similar' to the local naturally coloured water. However no analytical details were presented. Buckley et al. (1987) found that the concentration of humic acids in runoff from moorland at Llechweddmawr, Wales, was much

higher from ploughed areas. They also observed how following a storm event at Anglers retreat, colour was significantly lower from areas of soft ploughing, where furrows were close to contours and drains stopped short of the stream. These observations suggest that undisturbed organic rich soil may also act as a filter, removing humics from organic rich runoff.

2.1.3 The chemical nature of organic colour

Previous research into naturally coloured waters has focussed on two areas. Research concerning methods of treatment for colour removal, and particularly into the methods of colour coagulation, has, understandably received considerable attention, with treatment procedures well documented by the early 1960's. However about this time further progress into treatment processes was increasingly hampered by ignorance of the chemical structure of the colour producing organics, and so a second area of colour research emerged. This development is traced.

Many authors note differences in physical properties, molecular weight and particle size of colour compounds, and these differences have been used to explain why, for instance, organic iron extraction is successful in treating one water, but not another.

Shapiro (op.cit) reported an average molecular weight of 456 on the basis of isothermal distillation data, and an average equivalent weight of 228 by titration in an aqueous system. However, Blount (1972) reported a molecular weight

range of 1000-5000 for aqueous humics from Florida rivers. Steelink (1977) differentiated between soil humic and fulvic fractions with respective molecular weight ranges of 5000-100 000 and 300-2000.

Natural colour has been reported by some authors as being in true solution, while according to others it exists as a colloidal dispersion. Saville (1917) using electrophoresis stated that organic colour is present as a negatively charged colloid. Christman (1929) analysing 32 naturally coloured waters reached the same conclusion, while Goryunova (1952) found the water of lake Glubokoe in Russia to contain 96 gm^{-3} of organic matter, mostly as high molecular weight fatty acids and colloidal complexes. Shapiro (op.cit) found that colour, as the salts of humolimnic acid was completely dialysable through cellophane membranes, and stated that colour is therefore in true solution, and is not colloidal. However, he does not state membrane pore size.

Black and Christman (1963), reported after membrane filtration and dialysis, that the majority of colour forming compounds lie in the range 0.035-0.01 μm. However, where Shapiro based his conclusions on observations from thirteen lake waters, Black and Christman based theirs on observations from just one source, a creek in Gainesville, Florida. Several commentators believe sample source to have a significant effect on colour composition.

Table 2.1 Claimed chemical composition of colour forming compounds in water.

Date	Author(s)	Process	Observations
1909	Aschan	Ferric chlorite precipitation	Colour molecule contains Carbon, Nitrogen, Hydrogen oxygen and is an acid similar to phenol.
1910	Dienert	Oxidation	Fluorescent material lost.
1928	Keiser	Alum addition, Oxidation.	Differentiated coloured water into two organic groups. (humic and fulvic?)
1955	Skopintsev & Kryova	Spectroscopy	Aqueous humics of soil origin. Colour intensity related to absorbance.
1957	Raudnitz	IR-spectroscopy	Colour has no phenols or aromaticity. Consists of dibasic polyhydroxy aliphatic acids.
1959	Wilson	?	Colour is fulvic acid. Believed no specific test would be developed as too many functional groups.
1963	Black and Christman	IR-spectroscopy	Colour solids are aromatic polyhydroxy methoxy carboxylic acids.

1966 Christman & Ghassemi	Alkaline CuO degradation	Colour molecule contains phenolic structures. Identified seven degradation products all found in wood soil and water.
1971 Schnitzer	Fractionation, Permanganate oxidation and GLC/MS	Colour compounds largely aromatic. Proposed a structure for humic and fulvic acids with properties consistent with known properties.
1977 Steelink	NMR spectra	Coloured humics are stable free radicals. Few phenols,but their oxidation leads to catalysis of polymerisation and inhibits electron transport.
1986 Connor	Ultrafiltration dialysis and IR Spectroscopy.	Humic acids are not discrete molecules but are in dynamic equilibrium with each other. colour results from double bonds aromatic rings and phenols.
1988 Ren	IR and UV-vis spectroscopy with SEM,HPLC	Strongly polar aromatic compounds with phenolic acid derivatives. Material in suspension is ester derivative of aromatic carboxylic acids or their metal complexes.

Evidently there is confusion over the physical characteristics of colour, however there is considerable agreement over its chemical and spectral properties (table 2.1), conclusions being drawn from many studies of soil and aqueous humics from a variety of sources.

Aschan (1909) carried out the first extensive study on colour compounds, analysing waters from six Finnish lakes and rivers. After precipitation with Ferric chlorite, analysis of the humic material showed an average Carbon content of 44.99-54.1 %, Hydrogen 3.86-5.05 %, Nitrogen 1.46-4.23 % and Oxygen 38.76-47.93 %. He concluded that these materials were acids of similar strength to phenol. Dienert (1910) detected fluorescent material in natural waters and noted that it was lost on mild oxidation. Keiser (1928) differentiated natural water organics after observing that aluminium sulphate removed more oxygen-oxidizable material than chlorine-oxidizable material.

Most analysts report similar chemical composition of colour compounds, with the same elemental composition, percentage of carbon, hydrogen and oxygen. Nitrogen has consistently been found in low levels and was previously attributed to experimental contamination. However, it now appears that the presence of Nitrogen in colour compounds is real and present in several different types of molecular structure (Fuchsman 1980).

Skopintsev and Kryova (1955) stated that aqueous humics of

soil origin are responsible for coloured waters. They found a linear relationship, between the coefficient of extinction (absorbance) and colour intensity (fluorescence). Raudnitz (1957) isolated humic acid from rhododendron leaves, and, using IR-spectroscopy, showed the presence of hydroxyl and carbonyl groups. From his analysis of humic materials Shapiro (op.cit) concluded that colour molecules contain no phenolic structures and are largely dibasic polyhydroxy aliphatic acids. He supported this conclusion by presenting IR spectra with little indications of aromaticity. However, Black and Christman (op.cit) conducted qualitative spot tests on coloured waters from a number of sources. On the basis of these tests and IR-absorbtion data they concluded that colour solids were aromatic polyhydroxy methoxy carboxylic acids.

Research by Christman and Ghassemi (op.cit), and more recently by Schnitzer (1971), tend to support the view that colour compounds are predominantly aromatic. Christman and Ghassemi conducted alkaline-CuO oxidation of humic material and identified seven degradation products. After evaluation of the effects of the oxidation technique on model compounds they stated that their results proved conclusively the presence of phenolic structures in the colour macromolecule, and proposed a hypothetic structure. The degradation products; vanillin, vanillic acid, syringic acid, catechol, resorcinol, protocatechuic acid, and 3-5 dihydroxybenzoic acid were all found in both water, soil and wood extracted material, and is the

most conclusive evidence to date to support the view that discoloured water results from the leaching of soils and their organic decomposition products.

Schnitzer (op.cit) has also presented hypothetic structures for colour macromolecules, and used waters from a very much wider range of sources than Blackman and Ghassemi. Using non-degradative fractionation and permanganate oxidation, both followed by GLC/MS, he proposed structures for both humic and fulvic acids. These structures are consistent with known properties of humic materials such as base exchange, protein affinity, free radical content, metal chelation and, due to its open structure, the adsorption of numerous materials such as alkanes and substituted hydrocarbons. These water insoluble substances have been shown to be liberated upon the methylation of fulvic acid and suggest the presence of hydrophobic cavities.

Steelink (op.cit) has used NMR spectroscopy to study humic acids. He notes that humic acids are stable organic free radicals whose spin content increases with pH. He attributes this property to air oxidation of para or ortho-diphenolic to quinhydrone structures. Although there are few diphenol structures in humic acid, their oxidation to quinhydrone imparts a number of properties to the molecule, including catalysis of polymerisation and electron transport inhibition. Wilson (1959) stated that coloured materials in water are fulvic acids, and believed that no specific chemical test would be developed because of the diversity of functional groups present.

However, he believed a quantitative estimation based on UV-absorbtion spectra was possible.

From fractionation and degradation studies, Hayes (1987) concluded that humic substances consist of both aromatic and aliphatic groups. A core of carboxyl, phenolic, alcoholic hydroxyl and methoxyl groups is surrounded by carbohydrates and peptides in a random coil structure. The orientation of this structure allows inter and intra-molecular hydrogen binding to take place when the pH of the humic acid solution is lowered. This causes shrinkage of the coil structure and eventually its precipitation. Fulvic acids do not precipitate due to the abundance of polar groups in the structure which can be solvated. However they can hydrogen bind to humic acids, but these bonds tend to be weak, allowing fulvic acids, and to a lesser extent humic acids to be leached during periods of high rainfall.

Tipping (1987) has demonstrated how the solubility of soil humic substances is governed by their net electrical charge, the greater the charge the more soluble the humic substances. Using a description of ions between the diffuse double layer surrounding the soil particle and the bulk solution, and the complexation by humic substances of protons, aluminium and calcium ions, he was able to calculate the net charge on the humic macromolecule, and so predict its aqueous solubility.

2.1.4 The contribution of iron to water discolouration

Christman (1970) reported that 15-25 % of colour in natural waters was due to fulvic acid, and 75-85 % to humic acid. However, there is evidence that iron-humate complexes are the real colour producers.

Iron has received much attention with respect to water quality, as in natural waters ferric iron has been found in concentrations up to 100 times the theoretic value dictated by pH and redox potentials. An explanation for this has been sought in the relationship between iron and the dissolved or organic colloidal matter. Many authors note that waters rich in filterable iron are high in both colour and organic matter, the colour largely being organic. Indeed, iron 'in solution' is often referred to as organic iron.

Aschan (op.cit) and Aarnio (1915) both found that coloured water would not produce a precipitate on the addition of ferric iron if the ratio of iron to colour was carefully chosen. Gruner (1922), using filtered peat samples was able to solubilise iron in what he believed to be a ferric colloidal compound. The actual nature of the soluble iron was not defined.

In a study of naturally coloured waters Hem (1960) concluded that high concentrations of iron were held in a different manner to very low concentrations. Shapiro (1964) proposed two mechanisms by which iron is held by organic acids. The first is the formation of a soluble

(ferric) complex or chelate with the organic acids, and the second is as peptized oxyhydroxide sols. Theis and Singer (1973) report that humates can chelate 1-17 % of their own weight of metal ions, and that fulvic acids form tighter bonds than humic acids. Martin et al., (1976) reports on catastrophic fish kills in Florida after the flushing of humic acids following heavy rains. The fish kills were claimed to be due to massive algal blooming, a result of either chelated iron promoting growth, or the binding of phytotoxic copper, which is more firmly bound than iron. Shapiro found more iron held in solution at higher pH values than could be accounted for by chelation alone. He suggested that iron is held in solution as the result of ferric hydroxide precipitates being dispersed by attachment to organic acids. He termed this a protected colloid. However, Shapiro believed chelation to be an accessory mechanism to peptisation, playing an important role only when the ratio of iron to colour is high. Jirgens and Straumanis (1962) showed how in many cases chelates formed between metal hydroxide precipitates and organic poly-hydroxy peptising agents.

From numerous ultrafiltration studies, Lamar (1968) concluded that there is a wide range of colloid size, and that much of the iron is retained by coarse particles of organic matter as colloidal sols, probably in the form of ferric hydroxide or oxide under natural conditions. Lamar claims that 50 % of the colour is due to iron-humates of particle size less than 0.01μm , and that most of the

total iron does not contribute to the colour. Analysis of many highly coloured surface waters showed no consistent direct relationship between colour intensity and iron concentration in apparent solution. Lamar believed the inconsistency in the relationship to be due to the variable formation and precipitation of agglomerates of iron and organic matter as influenced by pH, availability of iron, concentration and availability of inorganic ions, contact period, and possibly by competition among cations.

2.1.5 Water discolouration and catchment hydrology

The effectiveness of decomposition in colouring waters depends on the quantity of material undergoing decomposition and the rate of decomposition, or where decomposition has ceased, on the quantity of decomposition products. The global distribution of peatland, a major source area for discoloured water is shown in table 2.2.

As colour is produced in situ, running waters subject to changes in rainfall and runoff, will exhibit considerably more variation in colour than lakes. Discharge rate then, is one of the major factors influencing the concentration of dissolved constituents in river water. The analysis of dissolved substances in runoff, and their relation to discharge aids in the identification of their source and the processes resulting in their release. An inverse trend between solute concentration and discharge has been described for many rivers. In times of increasing discharge, with all other factors affecting river

chemistry constant, this is to be expected. Baseflow, usually rich in solutes is diluted by interflow and surface flow, which have shorter residence times in the catchment, and hence a shorter period in which solution reactions can take place. Indeed, using chemical mass balance equations from small catchment runoff, Johnson et al., (1969) Pinder and Johns (1969) and Nakamuru (1971) obtain estimates of the proportion of baseflow in runoff.

Table 2.2 Global distribution of peatlands.

Country	Peat resource (ha)	Land surface(%)
Canada	129 500 000	12.98
USSR	71 500 000 *	3.19
Finland	10 000 000	29.67
USA	7 500 000	0.82
Norway	3 000 000	9.26
UK		
Scotland	821 381	10.70
England	361 690	2.80
N.Ireland	240 000	17.80
Wales	158 770	7.50
Total	1 581 841	6.60
Sweden	1 500 000	3.33
Poland	1 500 000	4.81
W.Germany	1 129 000	4.54
Iceland	1 000 000	9.71
Indonesia	700 000	0.36
E.Germany	489 000	4.52
Cuba	200 000	1.75
Japan	200 000	0.54
Eire	172 000 *	2.50
N.Zealand	166 000	0.62
Hungary	100 000	1.07
Netherlands	100 000	2.44
Denmark	60 000	1.39
France	60 000	0.11
Italy	60 000	0.20
Czechoslovakia	33 000	0.25
Austria	22 000	0.25
Rumania	6 000	0.03
Israel	5 000	0.24
Others	400 000	-

(* = Exploitable reserve, so is underestimate of resource). Derived from: Moore and Bellamy (1974).

Crisp (1966) investigated the variation in runoff chemistry from an area of Pennine moorland. He noted that concentrations of some elements tended to vary with discharge. Potassium and Phosphorous were related to high discharge, and Calcium to low discharge. He noted that other elements, namely Sodium and Nitrogen had no obvious relationship with discharge. Crisp made no attempt to account for his observations.

The output of organic carbon from Hubbard brook watershed, New Hampshire was studied by Hobbie and Likens (1973). They found concentrations of dissolved organic carbon and dissolved plus fine particulate phosphorous changed little with discharge, while concentrations of fine particulate organic carbon were strongly dependent, particularly during periods of high flow. However, these results were based on monthly totals and so could not distinguish between low flows and storm events.

Glover and Johnson (1974) described measurements taken on the River Tyne, UK, demonstrating that the concentration of certain dissolved constituents; termed the chemograph by Davies (1971), tended to lag behind associated changes in discharge, and that the lag time increased progressively downstream. They noted that the chemographs for colour, which they attributed to humic acids from upland peat moors, calcium and bicarbonate had the same lag time. They explained the phenomena of lag time on the basis of kinematic wave theory. However, Walling and Foster (1975)

pointed out that the simple dilution of base flow by flood water and the resultant effects on the differential between flood wave velocity and mean wave velocity are only two of the many controls on the nature and timing of solute concentration in runoff. They point out that the several pathways between the input of precipitation and the resultant channel flow must be considered, and that the various rates of solute pick-up will determine the precise nature of the chemograph.

Hall (1971) believes that over long periods, solute concentration discharge relationships may be obscured by non-random diurnal or seasonal fluctuations due to biological or chemical processes. Keiler (1970) found that the inclusion of soil moisture deficit and water temperature in a regression analysis of variation of dissolved constituents did not greatly improve the level of explained variance. However, Edwards (1973) notes that trends in concentration may better be investigated by time series analysis rather than with discharge as the independent variable. He also points out that only a small proportion of the variance in concentration may be explained by discharge where there is variable geology, land use and where man is active.

Many authors have noted how, particularly during the autumn months, the decrease in a solutes' concentration may be preceded by a rise in concentration, or an initial drop may be followed by an increase, before a subsequent

decrease. This has been termed the 'flushing effect' by Edwards (1973) and Walling (1974), accumulated solutes being flushed into the stream channel by initial phases of storm runoff. Walling and Foster (1975) observed this flushing effect on Calcium, Sodium and Magnesium in their study of small catchments in Devon, UK. They note how the shortest chemograph lags are associated with he highest stream flows, and suggest that chemograph lags are inversely related to antecedent catchment wetness and storm magnitude. During periods of low soil moisture status the upper soil horizons and ground surface will contain accumulations of soluble materials which are readily flushed by storm runoff. The solute content of the storm runoff reaches a minimum towards the end of the event when solute supply has been exhausted and before runoff with longer residence times feeds the recession limb of the hydrograph. The supply of readily soluble material is likely to have been depleted by previous storm events during conditions of high soil moisture.

Thus the chemograph lag can be predicted to a reasonable degree by discharge, measures of antecedent moisture status, catchment area (Walling and Foster 1975) and by mineral solubilities and position in the vertical profile of the catchment deposits. Mclaughlin and Johnson (1983) were able to demonstrate a significant drop in organic acid content down a Welsh forest soil profile, but did not measure colour directly. Boon et al., (1988) observed how more severely coloured waters originated from catchments

with large areas of flush zone peats and areas of erosion. They speculated that this was due to increased activity of aerobic bacteria during the relatively warm summer period. A detailed account of runoff characteristics of small peat covered watersheds is presented by Conway and Millar (1960) for the English Pennines and by Bay (1969) for the Minnesota peatlands, USA.

It has previously been pointed out that iron-humate complexes may be the primary colour producing agents in naturally coloured waters. Lamar (1968) highlighted the rôle of dissolved organic matter in iron complexing, concluding that variable quantities of Iron are held in apparent solution by complex organic acids. Grieve (1984) examined the mobilisation of iron by dissolved organic matter, and like previous authors (Fisher & Likens, 1972; Reid et al., 1981; Foster and Grieve, 1982) found both positively related to discharge. He also found iron transport to be limited at stream pH 8 and to be heavily dependent on organic matter complexing. The rôle of organic matter in iron mobilisation was confirmed by the strongly positive relationship between iron and dissolved organic matter. Greive found an autumn maximum for dissolved organic matter release and a pronounced decline in winter and attributed this to organic activity and flushing, while Foster and Greive (1982) presented evidence for dissolved organic matter flushing, released by decomposition and mobilised by rewetting following summer drying. Greive concluded that since iron mobilisation is largely

controlled by soluble organic complexing agents such organic acids, then the variation in the iron-discharge relationship is a consequence of the variation in the dissolved organic matter-discharge relationship. Greive also commented on the possibility of a seasonal variation in the complexing power of dissolved organic matter, given the varying relationship between dissolved organic matter and iron. He pointed to seasonal variations in polyphenol content of canopy drip reported by Davies (1970) who argued for a summer-autumn maximum in iron mobilisation in podzols.

2.1.6 Water discolouration and reservoir processes

Studies of artificial lakes or reservoirs principally concerned with yellow-organic discolouration are limited. However, in recent years with the advent of acid deposition as an issue of prime importance on the environmental agenda, many reservoir studies have been conducted, largely in Scandinavia, where the inclusion of water discolouration has become integral.

Gjessing and Samdal (1967) investigated the effect of impoundment on water colour. For the Trehorningen watercourse, Norway, with a chain of four lakes, they showed how colour decreases down the chain, both in the lakes and the brooks between them, and how in the recently dammed lake at the chains end, a marked increase in colour was observed. They concluded that the colour increase was due to extended peat submergence and speculated that the

extraction of humic material, complexing with metals or adsorbed on to minerals produced the colour. They attributed the decrease in colour in and between the lakes to a natural self purification process, related to the influence of sunlight, stream bed mineral composition and 'various biologic processes'. For a range of catchment size no correlation between storage time and colour was found.

Finnish artificial lakes are mainly located on peatlands and are strongly regulated. These reservoirs, which have a mean depth of less than 3m, are drawn down in April until they are almost empty, then once they are filled by the spring floods, attempts are made to keep the water level high until the following year. These exceptional properties; large fluctuations, short residence times and a peat bottom, affect the lakes stratification and biology, and have been the subject of numerous studies (eg Kleemola, 1967; Vogt, 1971). Typical features of these waters are high colour, iron and COD, with up to 80% oxygen saturation during open water, falling to near zero with ice cover. Vogt (op.cit) noted that new reservoirs had characteristically low Oxygen content and high values for Carbon dioxide, colour and COD, which after several years began to fall. However, he was unable to demonstrate any clear long term trend due to large annual fluctuations, and could not estimate the aging rate of new reservoirs built on peatlands.

Kenttamies (1980), in his study of Finnish reservoirs, examined trends in water chemistry and their relationship

to physical reservoir characteristics. He found strong biological consumption of Oxygen caused by high dissolved organic matter levels on the reservoir bed and in water entering the reservoir. Once the Oxygen in the hypolimnium became exhausted, large amounts of iron and Phosphorous passed into solution from the bottom. Kenttamies observed this effect all year round, but noticed that it was exacerbated in winter when water was drawn off the epilimnion, in preparation for the spring floods, thus increasing the proportion of the Oxygen deficient hypolimnion in the total water mass. Kenttamies used regression analysis to determine connections between the physical characteristics of the reservoir and the changing chemical properties of the water caused by residence times, but found no significant relationship for either colour or iron. However, using factor analysis to examine the influence of physical reservoir properties and inflowing water chemistry on outflowing water chemistry, he was able to demonstrate the importance of suspended solids and high oxygen deficiency in accounting for colour. Suspended solids chiefly explained the concentration of outflowing iron. Kenttamies results supports the theory that colour production within the water body is due to iron-humate complexes. Iron was the only metal-ion monitored by Kenttamies, so the potentially important rôle of other metals, for instance colour precipitation by aluminium flocculation, was not studied.

The geographical distribution of trace metals in relation

to acid deposition and water quality in 59 Swedish lakes was studied by Borg (1987). He tested a large number of hydrological and water chemical variables in a search for relationships with trace metals. He also presented evidence for higher rates of acid deposition in southern Sweden. Borg demonstrated that, beyond metal mobilisation within individual lake catchments, acid deposition was of limited importance in determining the geographical pattern of trace metals. He concluded that lake water pH, which was negatively correlated with aluminium, manganese and zinc, and lake water colour, which was positively correlated to iron, manganese, aluminium and lead were of greatest importance in determining trace metal distributions. Borgs' results place particular emphasis on the relationships between water colour and iron and aluminium ions.

Many authors have noted an increase in the transparency of lakes following acidification, which has been attributed to the input of cation acids, mainly inorganic aluminium species released by watershed acidification. There appear to be two mechanisms. The first involves the co-precipitation of humic substances with aluminium hydroxide. This would result in reduced dissolved organic carbon which has in fact been observed by both Almer et al.,(1978) and Dickinson (1980) for numerous lakes. The Second mechanism involves changes in the spectral properties of the dissolved humic substances during acidification. This is most likely due to cleavage of high

molecular weight humics, which would result in no overall decrease in dissolved organic carbon levels. This has been observed by Schindler (1980) in several Canadian lakes undergoing acidification. Both these colour reduction mechanisms have recently been validated by Steinberg and Kuhnel (1987) using Gel permeation chromatography and cation addition. They confirmed their results by the unrealistically high addition of Zinc, which had no effect on colour reduction.

2.1.7 Conclusion

The discolouration of fresh water by natural organic material is common throughout many parts of the world, particularly the USSR, USA, Canada, Scandinavia and the UK. Coloured water is objectionable to consumers due to its unaesthetic appearance and for the adverse effect it has on several major industrial groups. More seriously, there seems little doubt that the chlorination of potable water can result in mutagenesis of colour forming compounds. Such mutagens are potentially carcinogenic.

There is general agreement that colour in water is due to the leaching of dissolved organic matter from leaf litter and soil in drainage basins. It is thought that the humic fraction of dissolved organic matter, the most abundant macro-molecular material on earth, gives rise to colour in water. Humic materials have been defined as 'a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterised as

being yellow to black in colour, of high molecular weight and refractory' (Aiken et al., 1985). These substances do not belong to any unique chemical entity, as for instance proteins do, nor do they have any unique biochemical function. Thus as they cannot be defined in terms of function or structure they are defined operationally in terms of their solubilities in aqueous solutions. Humic substances consist of Humin, insoluble in water; humic acids, increasingly soluble with higher pH; and fulvic acids, water soluble at any pH. It is likely that fulvic acids, and to a lesser extent the higher molecular weight humic acids are responsible for discolouring water.

There does appear to be a particulate or colloidal fraction associated with coloured water, but this is inorganic and makes up only a small proportion of the total colour. The major colour forming fraction is organic and in true solution, consisting of both aromatic and aliphatic groups. These include carboxyls, phenols, alcoholic hydroxyls and methoxyl groups and possibly peptides and carbohydrates. Humic materials become more soluble, and hence water more coloured, when the bonds between them break down. Hydrogen ions tend to be the dominant cations neutralising the negative charge on the humic material. Thus changes in soil pH become important in controlling colour release.

Many authors have noted seasonal variation in dissolved organic matter, with a peak flow in the autumn months or following a spring thaw. This has been termed the 'flush effect', and has been explained in terms of rainfall, discharge, antecedent moisture and catchment area. However, few attempts have been made to account for spatial and temporal differences in water colour. The work of Boon et al., (1988) in the Elan valley, Wales is a notable exception.

There have been few direct studies of coloured water in reservoirs and it is not clear whether physical reservoir properties or inflowing water chemistry is chiefly responsible for changes in outflowing water chemistry. However, high levels of ionic iron and aluminium, and high suspended solids and oxygen deficiency have been strongly linked to incidences of high colour in reservoirs. These results were derived from the study of atypical lakes and reservoirs in Scandinavia and so may not be applicable on a wider geographical scale.

The discolouration of fresh water is thought to be due to the solubilisation of humic substances. The processes whereby these humic materials become soluble, are altered and transported within soil profiles, drainage basins and reservoirs are presently, only partially understood. Further investigation is required before discoloured flows can be accurately understood, predicted and managed.

2.2 Chemical and physical characterisation of locally coloured waters

In this section a physio-chemical analyses of locally coloured waters, is presented. Water samples were collected from the principal study sites in this research, including the Upper Nidd (SE 07 74), Upper Burn (SE 16 79) and Washburn (SE 17 56) valleys. These are largely simple analyses but are thought to be of sufficient sophistication to demonstrate similarities between locally coloured water and those detailed in the literature review. A limited number of samples are subject to more detailed chemical analyses, which compliment a study of the chemical structure of Upper Nidd coloured water, conducted by Ren (1988). All water samples were collected during an autumn flush period, except the Upper Burn samples which were collected over a one year period.

2.2.1 Colour changes during storage

The stability of water colour during storage was assessed. This was considered essential in anticipation of intensive field sampling and laboratory generation of coloured water. Water from Armathwaite Gill (Upper Nidd) was filtered (0.45 μm) and its colour measured, at 400 nm , within 2 hours of collection. This water was then divided into glass bottles for storage. Samples were not acidified. Colour stability was then assessed in terms of temperature and light intensity. Samples were stored at 8°C, 15°C, 20°C and 25°C in the dark. Additional samples were stored at 18°C

under bright tungsten lighting, fluorescent light, and with all light excluded. Four replicates were used at each treatment.

Results are illustrated in figures 2.1 and 2.2, and demonstrate that colour reduction of up to 28 % took place during storage. The most stable samples were those stored in the dark, and those at 8°C. These observations indicate that deterioration of colour is accelerated during storage by higher temperatures and light intensities. Therefore, if samples are to be stored for periods in excess of 48 hours, refrigeration is recommended. This reduction in colour is attributed to photo-oxidation and breakdown of the colour macromolecules.

These storage phenomena may also operate in reservoirs, particularly during summer months where higher air temperatures and longer daylight hours may contribute to photo-oxidation of coloured surface waters. Such processes would be more significant in reservoirs with large surface to volume ratios, and where storage periods can be prolonged.

2.2.2 Dilution behaviour

The behaviour of coloured water following dilution was assessed. Water samples of low (10 au m^{-1}) and high (82.6 au m^{-1}) colour were progressively diluted with distilled water with effectively no colour (0.1 au m^{-1}). The dilution of both samples was linear (figure 2.3). The

Figure 2.1 Effect of storage temperature on colour

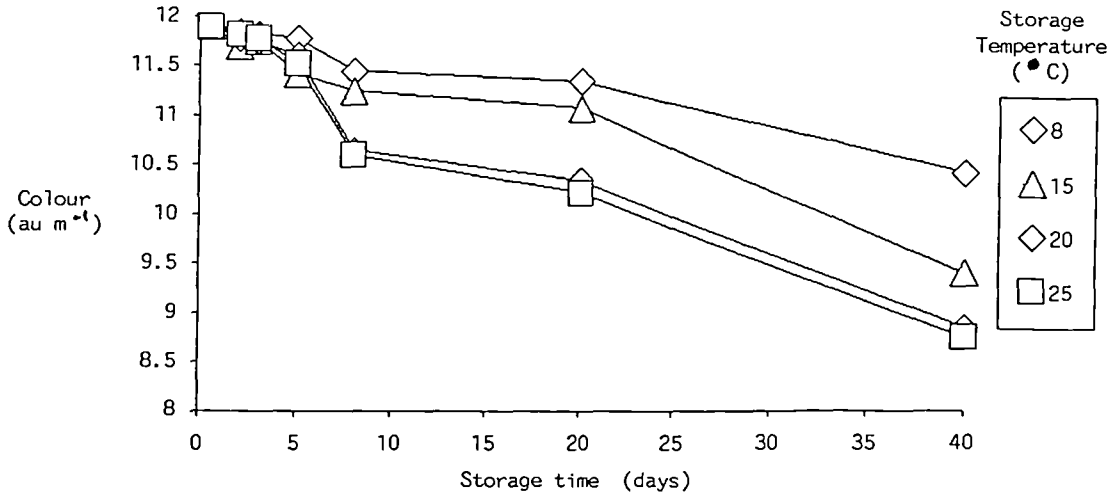


Figure 2.2 Effect of light intensity on water colour during storage

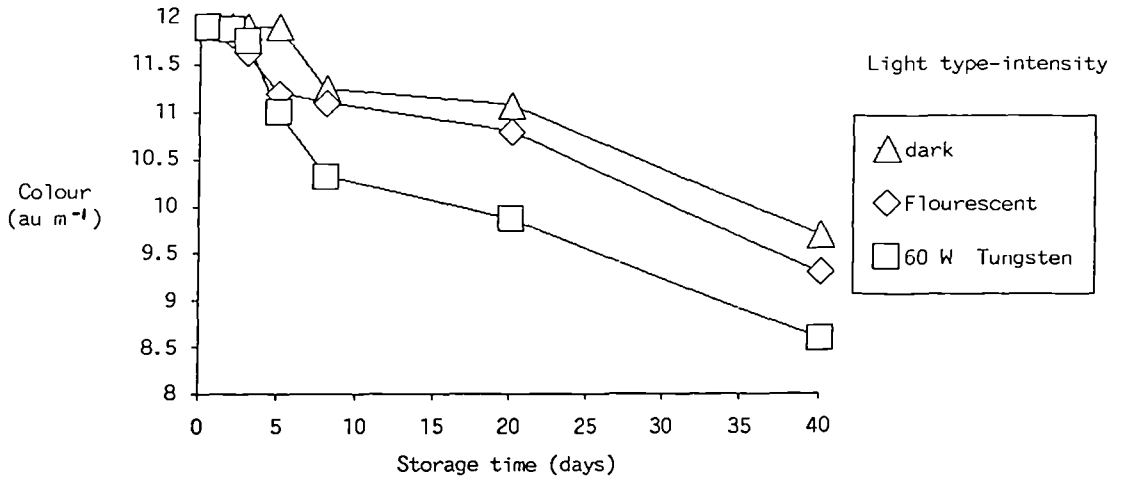


Figure 2.3 Dilution of low and high colour waters with water of no colour.

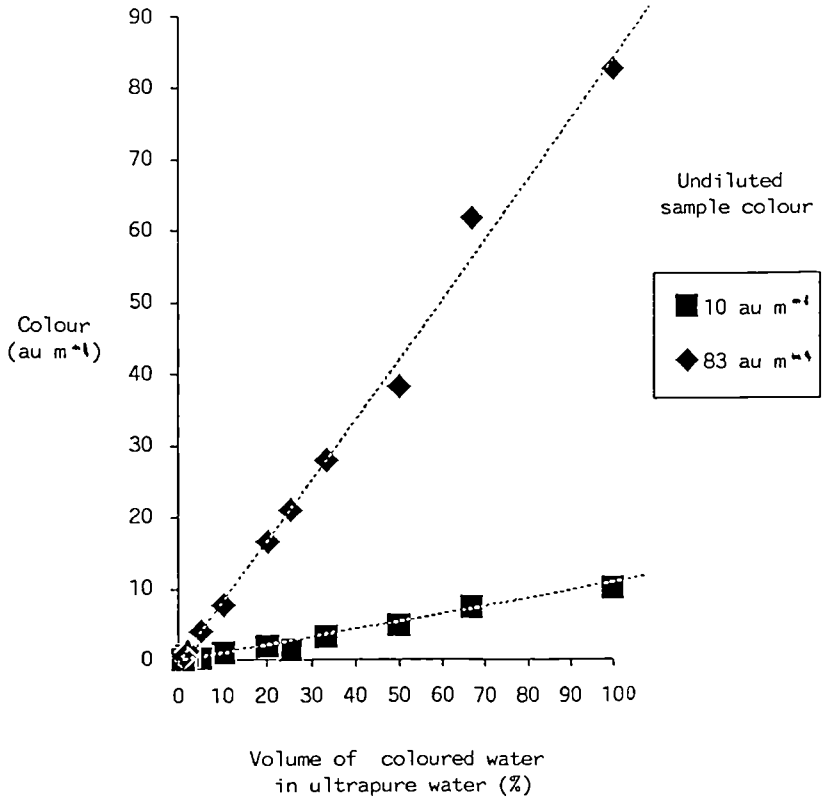
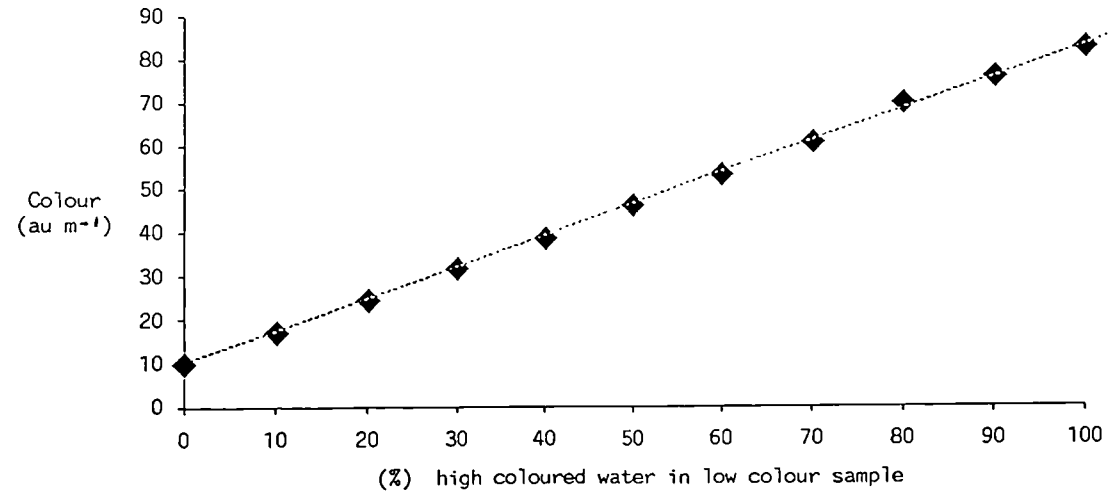


Figure 2.4 Dilution of low coloured water with water of high colour.



dilution of low colour samples with high colour water was also directly linear (figure 2.4).

This dilution behaviour implies that coloured runoff can be mixed with cleaner water to assist compliance with the EC standard. However, some coloured waters require great dilution to bring them to a level where they can be readily treated, and may better be discarded. For instance, $1x10^3$ l of HS14 ditch water (Upper Nidd) observed in excess of 1000 au m^{-1}, would need dilution by $6.7x10^5$ l of colourless water to bring it to EC standard. In such high colour areas large quantities of clean water are often not available for dilution purposes.

2.2.3 Titration of coloured water with acids and bases

Knowledge of the equilibrium chemistry of a solutions is useful in determining the chemical nature of the solution, and its reaction chemistry. Water can undergo dynamic changes resulting from the constant introduction of solar energy, and from the input of both organic and inorganic material. Information on the reaction chemistry of coloured waters cannot be used to accurately describe all the relationships between species as, in such complex systems as surface and groundwater flows, equilibrium is rarely achieved. However, equilibrium information can indicate the direction, speed and extent to which reactions would go if equilibrium were achieved, and whether certain chemical transformations are possible.

Samples of coloured water from Armathwaite Gill (Upper Nidd), were collected and filtered (0.45µm). These sample were then titrated against a strong acid (Hcl) and base (NaOH) and the change in solution colour measured. Further samples with low and high colours were titrated against a strong base only (0.025M NaOH) and the change in solution pH measured.

Typical titration curves are illustrated in figures 2.5 and 2.6. These titration curves are typical of a weak monobasic acid with a low degree of ionisation. That is, the colour comprises weak acids which are presumed to be organic in origin, presumably largely made up of humics and fulvics. These waters are also characteristicly low in conductivity. The highest colour samples were most acidic. Analysis of a large number of samples shows a strong negative correlation between colour and pH ($r=-0.5130$, $N=658$, $P < 0.001$). That is, high colour is generally associated with low pH. However, an increase in the pH of an already coloured solution, results in a further increase in colour. This colour increase is consistent with the solubilisation of the higher molecular weight organics such as humic acids. The initial colour is thought to result from the presence of lower molecular weight fulvic acids, which are water soluble, and therefore coloured throughout the pH range.

It has been demonstrated that water colour will increase if its pH is raised. This has implications for catchwater management. Coloured runoff is naturally acidic. Runoff

Figure 2.5 Colour change during acid-base titration

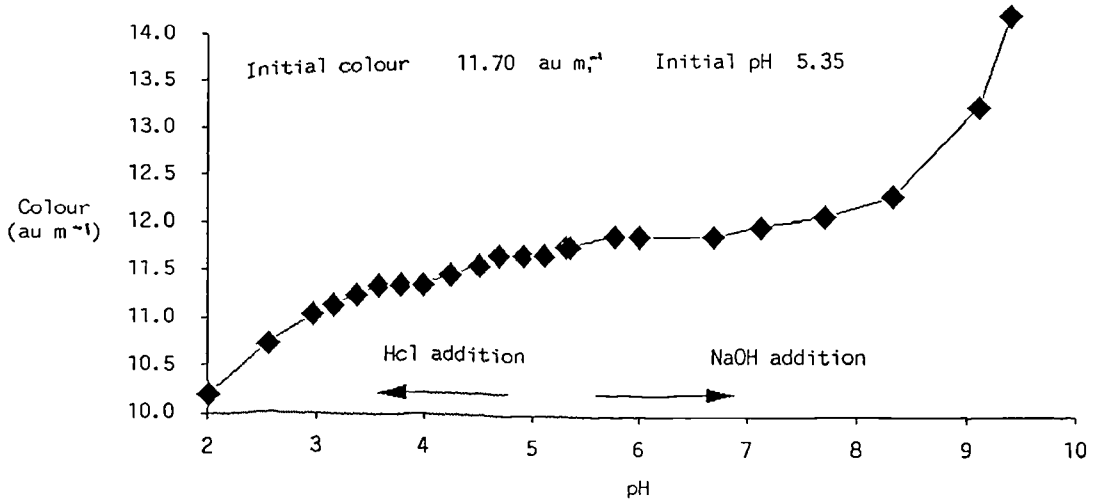
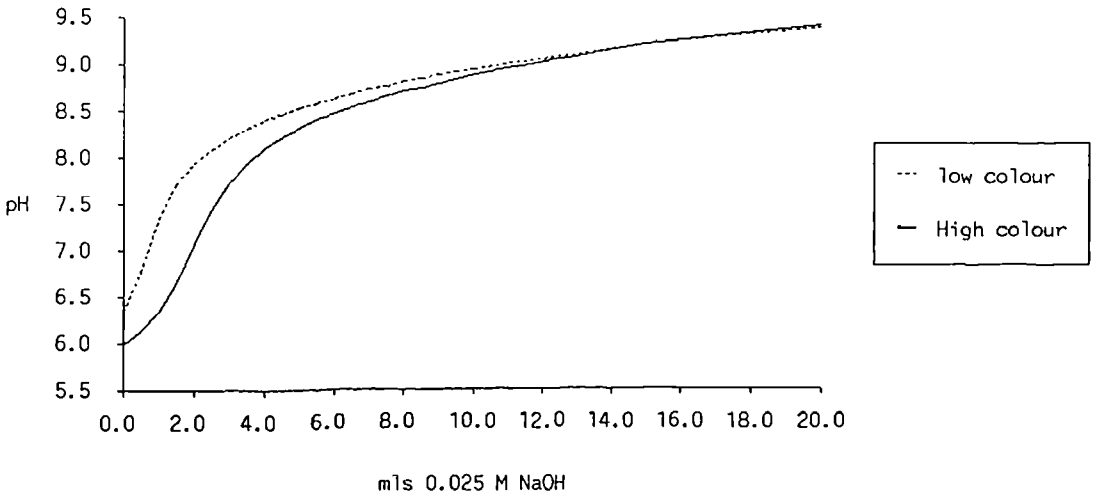


Figure 2.6 Change in pH of low and high colour water during base titration



low in colour is less acidic and nearer neutral due to the greater abundance of base salts and absence of colour producing organic acids. Therefore, if such lower coloured water is used to dilute waters high in colour, additional colour may be produced by making previously insoluble organics, such as the higher molecular weight humic acids, soluble, and therefore coloured.

2.2.4 Particle size analysis

Natural colour in water has been reported by some authors as being in true solution (eg. Shapiro, 1957) while according to others it exists as a colloidal dispersion (eg. Black and Christman, 1963). Three simple analyses to determine the size distribution of colour forming bodies were performed. Coloured waters were subject to rapid centrifuge, gravimetric settlement and ultrafiltration.

2.2.4.1 Centrifuge studies

Water from Scar House reservoir (Upper Nidd), with an initial colour of 12.1 au m^{-1} was subject to centrifuge up to 4000 rpm for 15 minutes. This water was first filtered (0.45μm) to remove large suspended sediment that would mask any colour change, thus only those chromophores contributing to 'true' colour were considered. After centrifuging, small aliquots were drawn of the top and bottom of the centrifuge vessel, and their colours compared. Results are presented in table 2.3.

These results are not conclusive. It is seen that

after centrifuging colour differentials do exist, but the degree of experimental error could not allow these small differences to be attributed to the colloidal nature of colour. However, it is evident that the largest colour differential exists after maximum centrifuging, and that at low speeds, no colour differential exists. An ultra-centrifuge, with higher centrifuge speeds, may have shown greater differences.

Table 2.3 Colour (au m^{-1}) change following centrifuging.

rpm	Time (mins)	Total revs.	Colour (top)	Colour (bottom)	Colour differential
0	0	0	12.1	12.1	0.0
1000	5	5 000	12.1	12.1	0.0
2000	5	10 000	11.8	11.9	0.1
3000	5	15 000	12.1	12.0	-0.1
4000	5	20 000	11.9	12.0	0.1
4000	10	40 000	11.9	11.9	0.0
4000	15	60 000	11.9	12.2	0.3

2.2.4.2 Gravimetric settlement

The effect of long term gravimetric settlement on colour was studied. Coloured water (0.45µm filtered), was placed in eight, 60 cm glass columns, and stored vertically in a cool dark environment for up to 100 days. Periodically, the entire contents of one water column was drawn off the bottom and directed into a succession of sample bottles, so dividing the water column into a series of crude layers.

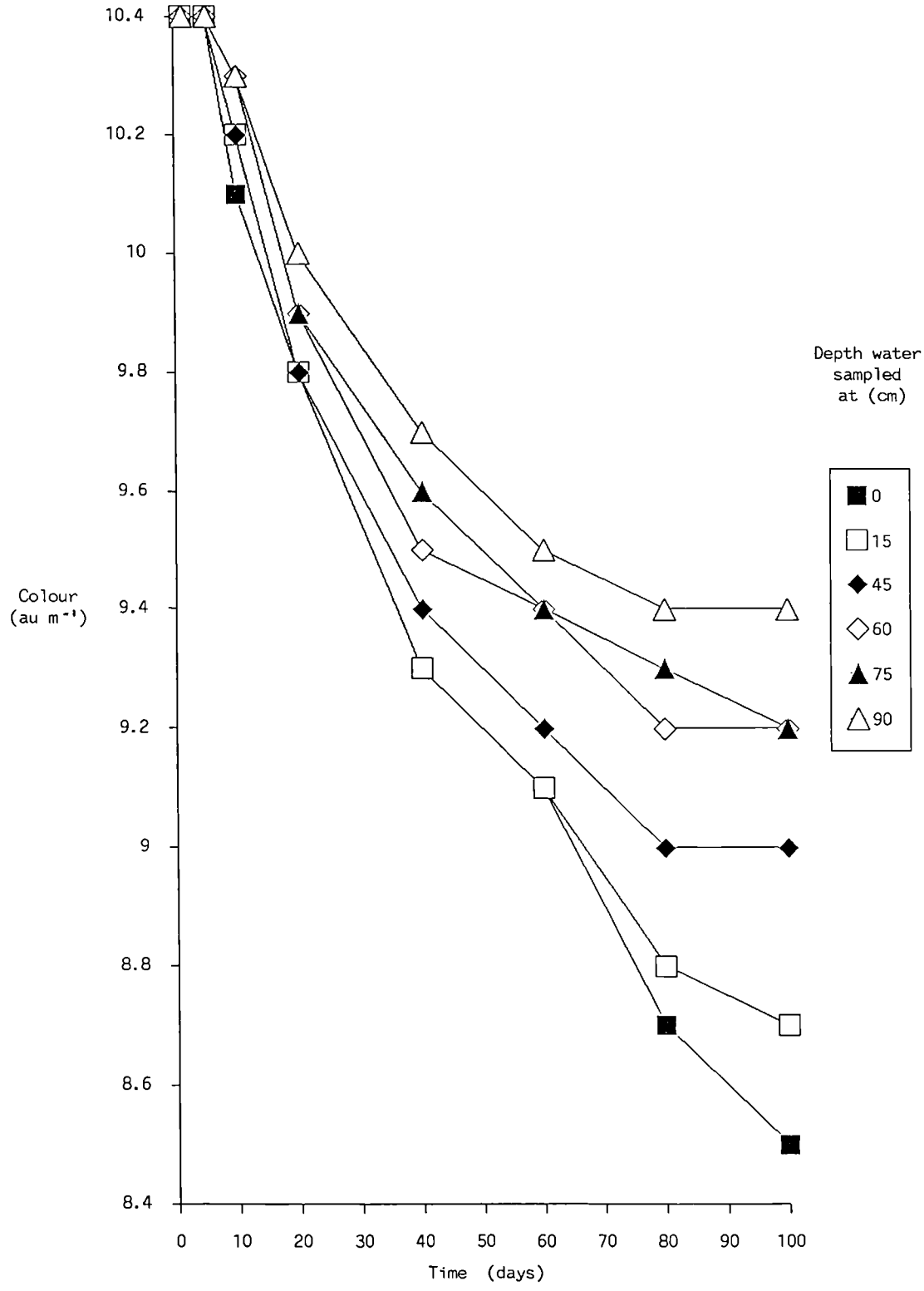
Results are illustrated in figure 2.7.

Colour levels are seen to decline gradually in all 'layers' throughout the experimental period. This decline is consistent with the photo-oxidation and breakdown of colour during storage as detailed above. However, colour decreases more rapidly in the upper layers and suggests that colour producing material is settling under the influence of gravity. Although the colour differential is small (10 %), and unreplicated, the consistent increase in colour with column depth does suggest that colour exists as a colloid.

2.2.4.3 Ultrafiltration

A more effective means of determining whether colour is colloidal, or in true solution, is achieved by passing coloured water through successively smaller pore spaces, and observing the drop in colour - ultrafiltration. Raw water was passed through a succession of filters with pore spaces of 1.0, 0.8, 0.65, 0.45 (standard size for true colour determination), 0.3, 0.2, 0.1 and 0.03 microns. All filters were cellulose nitrate membranes, with the exception of the 0.1 and 0.03 micron filters, which were composed of polycarbonate cellophane. Three types of water were analysed. Water from Armathwaite Gill (Upper Nidd), with an initial raw water colour of 18 au m^{-1}, a peat extract water, with an initial colour of 30 au m^{-1}, and ultrapure water (treated by slow sand filtration, activated carbon and reverse osmosis) with virtually no detectable colour. Results are illustrated in figures

Figure 2.7 Colour decay within a water column.



2.8 and 2.9.

The coloured samples both lose colour gradually upon filtration to 0.1 µm (table 2.4). Both coloured samples lost between 14% and 17% colour with filtration up to and including 0.45µm . This illustrates the difference between true and apparent colour determinations and highlights the necessity for the use of a standard colour determination technique. After 0.1µm filtration both coloured samples had lost 23-25 %, of their colour. However, the majority of colour (>70%) was lost after 0.03µm filtration, and indicates that over half the colour of the samples was formed by bodies in the range 0.03 - 0.1 µm . A significant proportion (17-27%) of the colour was provided by bodies smaller than $0.03u^{-1}$. This is consistent with the work of Black and Christman (1963) for coloured waters from Florida, USA. They found that the majority of colour bodies lay in the size range 0.035-0.01µm .

Table 2.4. Colour reduction (%) on filtration.

Filter size (µm)	Armathwaite Gill	Peat extract
1.00	9.34	8.63
0.80	12.64	13.62
0.65	13.18	13.62
0.45	13.73	16.61
0.30	15.93	16.94
0.20	15.93	23.59
0.10	25.27	23.59
0.03	73.10	83.06

Figure 2.8 Colour change during ultrafiltration

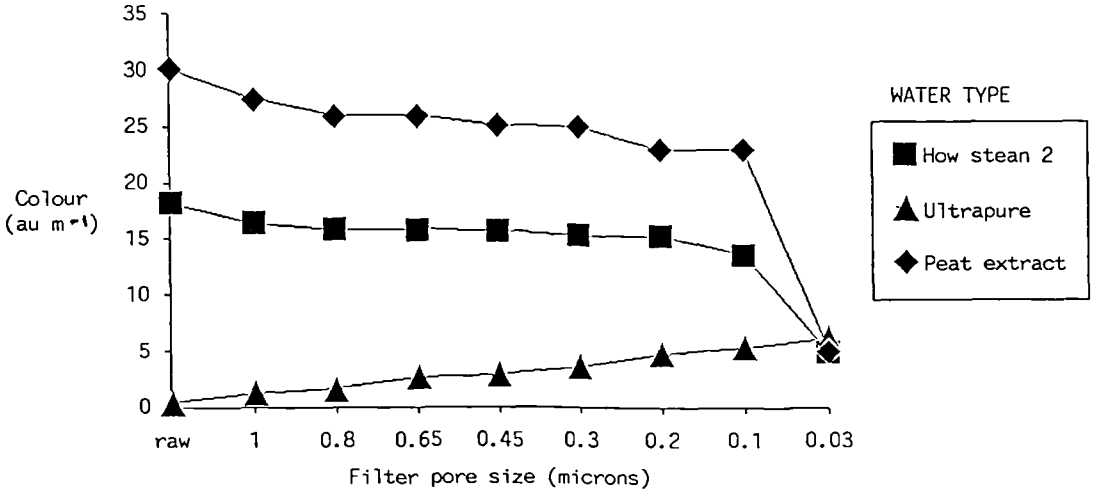
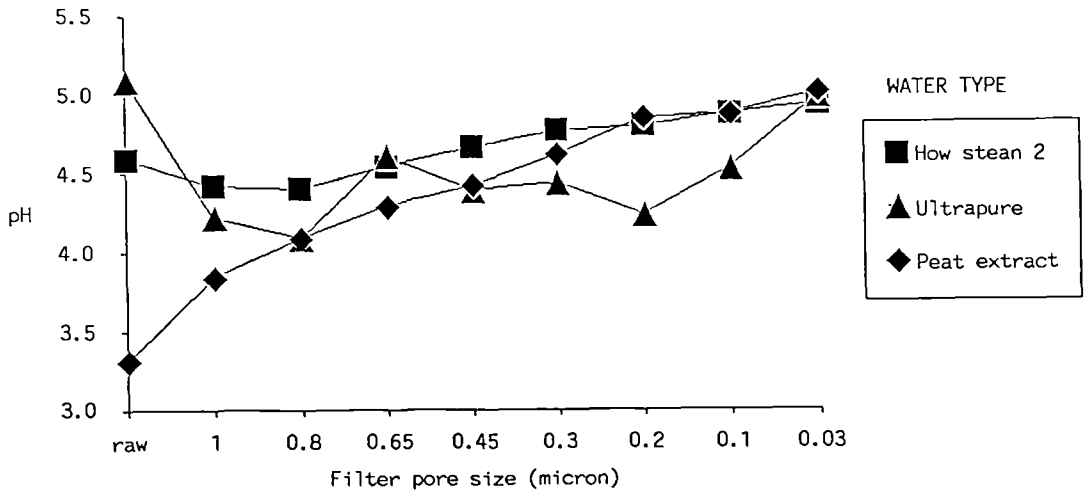


Figure 2.9 Water pH change during ultrafiltration



There is, to some degree, a relationship between colour reduction and pH. As colour is removed, the sample pH rises indicating that colour producing material is acidic itself. However the major colour drop at 0.03 µm is not matched by an equal rise in pH. This may indicate that the strongest hydrogen bonds with the colour molecule exist in that coloured fraction ≤ 0.03 µm . It is assumed that the act of filtration itself does not cause this pH rise as the ultrapure water exhibits no clear pattern of pH change on filtration.

The colour of the ultrapure water was seen to rise fractionally on filtration. This was attributed to small particles from each filter causing turbidity, not colour. However, experiment demonstrated that filtration of ultrapure water through 0.45 µm filters only, consistently added 0.3 au m^{-1}. This is a significant value in light of the EC standard of 1.5 au m^{-1}, irrespective of whether this addition is caused by colour or turbidity.

2.2.5 Typical ionic composition

An assessment of the relationship between the degree of discolouration and the concentration of major ionic species in water is a useful method of determining which species may incorporated in the chemical structure of colour producing bodies. Such an assessment may also indicate which catchment hydrological processes, operating to contribute particular species to runoff, are also important in removing colour.

Determination of the major ionic species in Upper Nidd and Burn waters was performed by atomic absorbtion spectrophotometry and ion Chromatography. Operating conditions and confidence limits are detailed in Appendix II. The correlations between colour and the concentration of several major ionic species is shown in table 2.5.

Table 2.5 Pearson correlations between colour and major ionic species for two upland gathering grounds.

Species	Upper Nidd	Upper burn
F^-	<u>-0.625</u>	-0.0677
Cl^-	-0.166	-0.2634
NO_2^{2-}	0.168	-0.1318
Br^{2-}	< L.D.	< L.D.
$H_3PO_4^{2-}$	< L.D.	-0.0950
SO_4^{3-}	0.183	-0.0880
Mn^{2+}	<u>0.360</u>	0.1234
Fe^{2+}	<u>**0.806**</u>	<u>**0.8146**</u>
Al^{3+}	-0.278	<u>**0.6132**</u>
Ca^{2+}	N/A	-0.2203
Mg^{2+}	N/A	-0.2502
N	84	658

$P <$ <u>0.01</u> $P <$ <u>**0.001**</u> N/A Not analysed

< L.D. levels below limit of detection

The strongest relationship existing for both catchment

areas is that between colour and iron. These relationships ($P<0.001$) are particularly strong considering the diverse and complex nature of the factors controlling species solubility between catchments. The agglomeration and precipitation of iron is affected by pH, iron availability, contact period, concentration and availability of inorganic ions, and the presence of competing cations. This then is strong evidence for the inclusion of iron within the structure of the colour producing macromolecule. The iron is likely to chelated with organic acids, or possibly peptised as an oxyhydroxide sol. Ren (1988) believed that free carboxylic acids on the aromatic ring could complex with soluble metal ions in water, and that the degradation of phenolic components, producing biphenols might complex metals, including iron, under oxidising conditions. This relationship that exists between colour and iron is particularly strong, given that iron forms tighter bonds with fulvic acid. The relationship is thus likely to break down with high colour samples, as these are most highly coloured due to the presence of humic acids, which do not form such tight bonds.

The strong correlations that exist between colour and iron, manganese and aluminium may also be indicative of solubilisation processes similar to that for colour. For instance, during the summer peat drying leads to oxidation. Under these conditions, iron (as ferric oxide or iron sulphide) and manganese (as manganese dioxide) are insoluble, in

stable oxidation states. Following rewetting of the peat, anaerobic conditions arise and reduction from Fe(III) to Fe(II) and Mn(IV) to Mn(II) takes place. These reduced forms are highly soluble and will be flushed out with water table rise and catchment runoff.

Rates of oxidation of Fe(II) and Mn(II) are not rapid, and so the reduced forms can persist in aerated water for some time. This is especially true when the water pH is < 6 for iron oxidation and < 9 for manganese oxidation. These pH constraints would be met in acidic peat areas.

These observations suggest that the high correlations found between colour and iron and manganese are not necessarily due to complexation of the metals with the colour molecule. Colour, iron and manganese may all exist in runoff following aerobic oxidation and anaerobic solubilisation, and are highly correlated as they have similar origins. That is, summer drying, followed by water table rise, and solute removal. Colour results from the solubilisation of organic acids, which act to lower the water pH, and so allow the soluble reduced forms of iron and manganese to persist in water.

These observations may be useful in determining the behaviour of colour under different circumstances. For instance, it is known that iron and manganese cause problems in stratified reservoirs (Morgan and Stumm, 1964). The reduced forms are released from bottom sediment and

are contained in the anaerobic hypolimnium. In autumn, stratification is disturbed, and the reduced forms pass into supply, and can cause problems until oxidised. Colour may be released from reservoir sediments and retained in the hypolimnium in a similar fashion. Such colour would pass into supply when the hypolimnium was disturbed, during autumn, and so contribute to the autumn colour flush.

2.2.6 FT-IR analysis

Water samples were analysed by Fourier Transform infra-red spectrophotometry. The advantage of FT-IR analysis is that aqueous samples can be scanned to determine functional groups in the sample. Normal IR scans would suffer interference from water molecules, so samples are usually made into solid discs. The process of producing these discs involves the physical isolation of the material causing colour and its incorporation into a KBr disc. This process is difficult, and there is no guarantee that only the colour producing material is isolated, or that it is not altered during the analysis.

Using FT-IR analysis aqueous samples are scanned 100 times with a resolution of 4 cm . A similar scan, of ultra-pure water, can then be automatically subtracted from the sample scan. This residual scan results from those functional groups found only in the sample. This analysis was performed for two samples; one highly coloured (35 au m^{-1}) from Armathwaite Gill (Upper Nidd) and one low colour sample (1.8 au m^{-1}) from an adjacent catchment.

Table 2.6 Transmittance (%) of low and high coloured samples using FT-IR.

Wavelength (cm)	High (35au m^{-1})	Low (1.8 au m^{-1})
1508	99.860	97.995
1523	99.700	97.745
1540	99.790	-
1542	-	97.205
1558	99.630	-
1559	96.760	-
1570	99.335	-
1605	98.465	-
1615	98.060	-
1621	97.880	-
1631	97.475	91.095
1635	-	91.370
1641	98.130	92.045
1646	-	91.810
1651	-	92.405
1653	97.815	-
1670	99.130	-
1680	99.565	-

The reduction in transmittance at a particular wavelength is proportional to the concentration of functional group at that wavelength. Comparison of the two residual scans shows that the functional groups causing colour only reduce transmittance by a small amount, (maximum of 9% with high

colour sample), and takes place in only a fraction of the spectrum, 1500-1700 cm . The full spectrum runs from 100-1720 cm . The differences between ultra pure water and the coloured samples are presented in table 2.6.

These spectra indicate that the colour of the samples studied may contain members of the functional groups amides, amines, alkenes aldehydes together with inorganic salts and their derivatives. However, the greatest reduction in transmittance is found in the aromatic and carboxylic acid regions. This tends to support the view of earlier authors who have suggested that colour is a derivative of strongly polar aromatic carboxylic acids.

Analysis of many more samples, with a broad range of colour would allow further isolation of the most common colour producing functional groups, and control for functional groups present in the samples but not contributing directly to colour. However, such an analysis is likely to indicate that colour results from the presence of many functional groups, all produced by the process of organic matter breakdown.

Further chemical analysis of coloured water, collected from one of the principal study sites in this research (Upper Nidd), was conducted (Ren 1988). These analyses included SEM, HPLC, UV-vis and conventional IR-spectrophotometry. The results indicate that colour producing bodies are strongly polar aromatic compounds with phenolic acid derivatives. The suspended material was thought to be the

ester derivatives of aromatic carboxylic acids or their metal complexes. Degradative fractions were believed to be catechol, resorcinol, protocatechuic acid and 3,5-dihydroxybenzoic acid, with up to ten compounds unresolved. These fractions were positively identified by Christman and Ghassemi (1966), who found them to be common to wood, soil and water. They concluded that the compounds responsible for colouring water, were of common origin, and that water was discoloured by the presence of the products of organic matter breakdown. This suggests that the Upper Nidd water is coloured by similar compounds that colour water throughout the world, and, moreover, that this discolouration is the result of the solubilisation of organic matter breakdown products.

2.2.7 Conclusion

These largely simple analyses were able to demonstrate the strong similarity of locally coloured water, collected from the principal study sites in this research, to those coloured waters, collected from throughout the world, described in the literature.

Approximately 25 % of the colour forming bodies were >0.1µm , 25 % <0.03µm , with 50 % in the range 0.03-0.1 µm . This supports the view that colour is not caused by any unique chemical entity (like proteins for instance), but that its origins are in 'humic substances'. These humic substances have a high molecular weight range, but cannot be characterised in terms of structure or function. These

substances are characterised in terms of their solubilities in aqueous acids and bases. Thus colour forming bodies exhibit a size distribution as demonstrated above, and so may exist in both true solution and colloidal states. However, what is clear, is that for all practical purposes, the greater proportion of colour likely to be found in runoff is not colloidal or particulate, but can be considered to be in true solution.

The exact structure of these colour producing bodies cannot be determined; they may exist as polymers, aromatic or aliphatic compounds, as coiled structures or as macromolecular charged colloids. However, it has been demonstrated that colour has no unique chemical structure, and it seems likely that the colour producing bodies can exist in all these states. Organic acids are believed to be largely responsible for water discolouration, particularly fulvic and humic acids. The terms fulvic and humic acids are used as a convenience, and to not describe any unique chemical entity. Fulvic and humic refers to long chain organics of broadly low and high molecular weights respectively. Humins are usually included in any categorisation of organic acids, but are not included here as they are insoluble in water at any pH, and are not thought to contribute to discolouration. There is also strong evidence that iron makes a significant contribution to water discolouration. Iron is thought to combine with the main organic component of colour, either by chelation, peptisation, or complexation. Whatever the mechanism, it is

known that tighter bonds are formed with fulvic acid fractions. These fractions are less coloured than humic acid fractions, but are more soluble and therefore more abundant in water.

The analyses of coloured water, collected from the principal study sites in this research, demonstrate that these coloured waters are similar in nature to those found in other parts of the world. No definitive structure has been identified, as no definitive structure exists. Colour in water is a composite of many functional groups and complexes. However, it has been demonstrated that coloured waters from different sources have many chemical attributes in common. In particular, the identification of several degradative products, all found in wood, soil and coloured water, (Christman and Ghassemi, 1966) indicates a common origin - organic matter decomposition. These products, found in coloured water from several different sources, including the Upper Nidd, and the broadly similar nature of coloured waters, suggests that the process of discolouration is likely to operate in a similar manner wherever discoloured water is found.

3. THE SPATIAL DISTRIBUTION OF DISCOLOURED RUNOFF

3.1 Aims and introduction

On a global scale, the spatial distribution of discoloured runoff is unknown. The World Health Organisation does not set a standard for coloured water, and consequently the collection of coloured water data is limited. Colour measurement tends to be restricted to developed countries where water discolouration is more readily perceived as a problem by local water resource agencies. Thus most coloured water studies have been conducted in the United states and Canada, the Soviet Union, and throughout Europe, particularly Scandinavia. Throughout the rest of the world single studies have been conducted in New Zealand (Timperley, 1985) and in parts of the Amazon river basin (Fittkau, 1964; Williams, 1968). There is little or no information on water discolouration for Africa and Asia (excluding the USSR). However, even in the developed countries the collection of coloured water data is often irregular and the data of poor quality.

From geomorphological studies net denudation rates have been calculated for the earths' surface. However, the extent of water discolouration in different regions cannot be interpreted from such data for two reasons. Firstly, the organic/mineral ratio is not constant in eroded sediments. Secondly the chemical characteristics of dissolved organic matter are affected by the availability of metal ions that can result in waters becoming more or less

coloured. The spatial distribution of these metal ions is not constant (Arnett, 1978).

Globally, significantly coloured runoff appears to be confined largely, but not exclusively, to areas from 40°N-65°N and 40°S-65°S, although data availability does make such a conclusion tentative. These areas have a temperate to cool temperate climate with mean monthly temperatures from above freezing to 30°C in summer and from -30°C to 5°C in winter. Mean annual precipitation ranges from 600 mm - 4000 mm.

At the regional scale there is a much greater spatial variation in the degree of water discolouration. The effects of temperature and precipitation, most significant at the continental scale, are replaced by more localised factors of relief, lithology, pedology and land use. Whilst water colour has been measured for a number of upland sites in the UK, there have been few attempts to explain water colour in terms of catchment characteristics. Notable exceptions are the work of McDonald et al., (1987) on the upper Nidd valley, north Yorkshire, and Boon et al., (1988) for the Elan valley, Wales. Consistent differences in sub-catchment colour were found in both study areas. These differences were attributed to organic rich and peat soils, and to land management practices, particularly ditching and burning. Interfluve peats, rare in the Upper Nidd, were also identified as a source of colour in the Elan valley.

In this chapter an attempt is made to identify colour source areas with respect to catchment characteristics. This is done at a regional scale, considering whole catchwater systems; at the sub-catchment scale, within just one catchwater; and at a micro scale, within a subcatchment. Determination of the relationship between runoff colour and catchments characteristics is an important first step in identifying the process(es) by which water becomes coloured.

3.2 Regional distribution of discoloured water

3.2.1 Methodology

In this section, an attempt is made to account for the variation in colour found between a selection of Pennine reservoirs. The forty six reservoirs and associated drainage basins studied were selected on the basis of availability of water colour data. This data has a frequency of at least one reading per week throughout the designated study period. The study area, illustrated in figure 3.1, extends over approximately 7000 km^2 and includes parts of the Yorkshire dales, North York moors and the Peak district. The reservoirs are listed in appendix I.

For each reservoir both true and apparent colour data, covering the period January 1986 to December 1988, was analysed. Mean values were calculated and used as the primary description of catchment colour. Further dependent variables, describing the colour variation for each reservoir were calculated. These were the standard

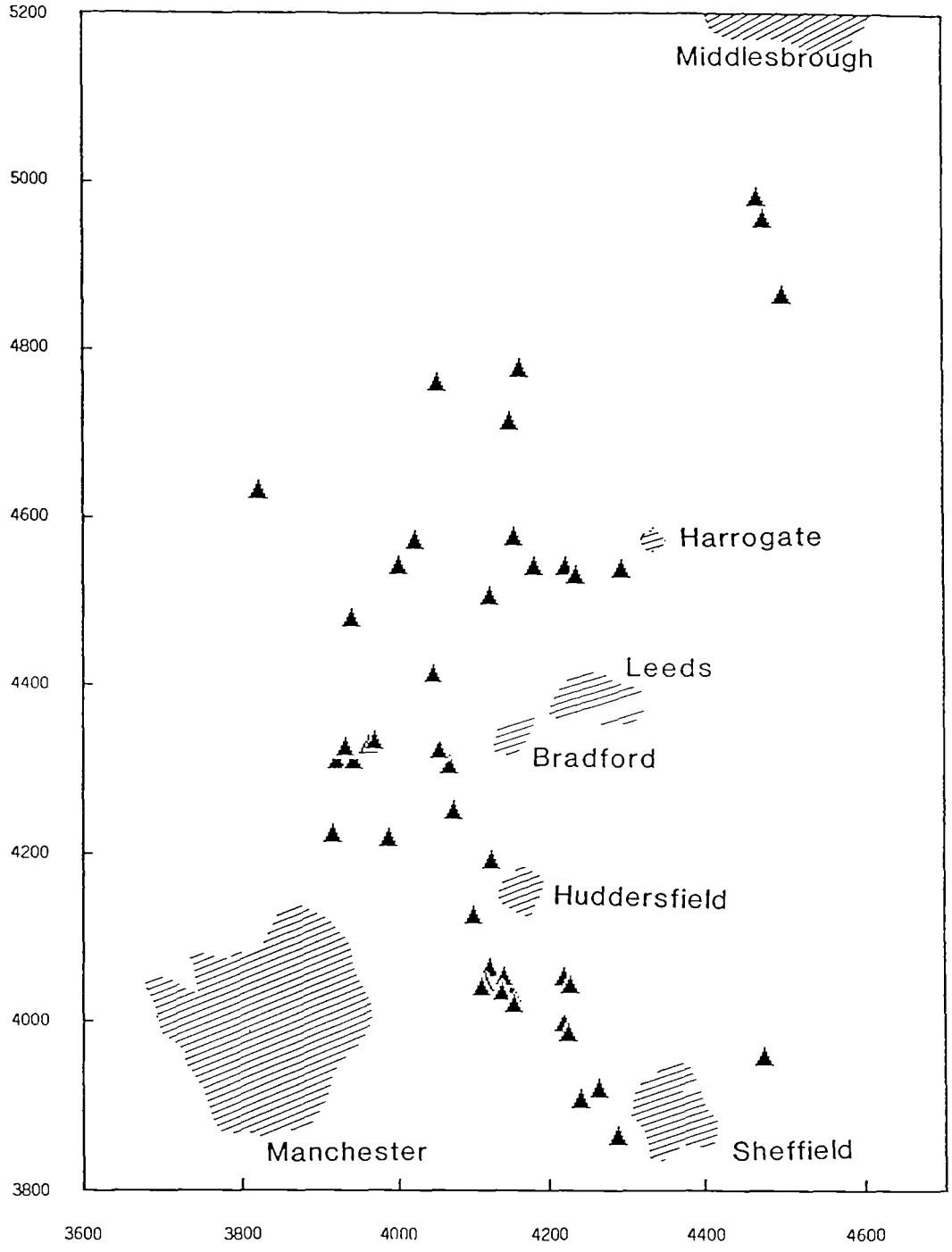


Figure 3.1 Location of reservoirs in regional analysis of the spatial distribution of colour

deviation, minimum, maximum and the colour range. A further dependent colour variable was calculated using true colour data only. This was termed 'high colour' and was calculated as the mean of all values in excess of one standard deviation. This variable was calculated as the maximum colour for each reservoir is defined by one observation only, and cannot accurately represent high colour periods. An analysis of high colour was performed as the temporal distribution of colour is known to be non-uniform; a significant proportion of the total annual colour flows during short periods.

Dissolved organic acids are thought to contribute significantly to water colour. Therefore water acidity, recorded as pH, may be a useful further indicator of colour source areas, and is included in the analysis. The water pH data covers the period January to December 1987.

Table 3.1 Relationship between True and apparent colour variables for 46 Yorkshire reservoirs, 1986-1988

Variables used to describe true and apparent colour	r
Mean	0.8343
Standard deviation	0.5793
Maximum	0.6608
Minimum	0.8201
Range	0.5591
	P< 0.01 P< 0.001

True colour data is preferred for analysis, as there is no interference by suspended sediment. However, the apparent colour data set was more extensive. Correlation of variables describing the true and apparent colour data were positive and significant (table 3.1) and it was felt that this justified the inclusion of apparent colour data in the analysis.

The independent variables used to investigate the spatial distribution of coloured water are shown in table 3.2. These variables are grouped under geology, pedology, drainage basin morphometry, reservoir morphometry, land use and local climate.

Table 3.2 Descriptive drainage basin characteristics.

(a) Geology (% catchment coverage by solid deposit).

80	Tournaisian and Viséan (Carboniferous limestone)
81	Namurian (millstone grit)
82	Lower Westphalian A,B (mainly productive coal)
94/95	Great/inferior Oolite
96	Cornbrash

Source: Geological Survey 1:625 000 Ten mile map (1979).

(b) Pedology (% catchment coverage by soil subgroup).

311a	Revidge (shallow acid peat)
421a	Stow (Typical non-calcareous pelosol)
541f/g/o/x	Rivington/E.Keswick/Malham (Brown earths)
542	Nercwys (Stagnogleyic brown earth)
631a	Anglezarke (Humo-ferric podzol)

651a	Belmont (Ironpan stagnopodzol)
652	Maw (Humus ironpan stagnopodzol)
711p	Dunkeswick (Typical stagnogley)
712a/d	Dale/Hallsworth (Pelo-stagnogley)
713g/h	Brickfield/Ticknall (Cambic stagnogley)
721a/b/c	Kielder/Onecote/Wilcocks (Cambic stagnohumic gley)
1011b	Winter hill (Raw oligo-fibrous peat)

Source: Soil survey of England and Wales, sheet three, 1:250 000. These soils are described in Avery (1980).

Winter rainfall acceptance potential(WRAP). WRAP class 1-5. Source:Soil survey special survey 11. (Farquharson, et al., 1978).

(c) Basin morphometry

East	National grid reference easting of basin centre.
North	National grid reference northing of basin centre.
Area	Basin area (Km^2).
Per	Basin perimeter (Km).
$Elev_{max}$	Highest point on the basin (m).
$Elev_{min}$	Lowest point on the basin (m).
BR	Basin relief. ($Elev_{max}$-$Elev_{min}$) (m).
BL	Basin length. Distance of line from basin mouth to point on perimeter equidistant from basin mouth in either direction (m).
Elgn	Elongation (Schumm,1956). (2x $Area^{0.5}$)/(BL x 1).
Cren	Crenulation (Miller, 1953). Relative perimeter

crenulation. (per^2/Area)/(4l).

RR Relief ratio (Schumm, 1956). BR/BL.

RRf Relative relief (Melton, 1957). Area/Per.

DD Drainage density (Horton,1945). TCL/area.

GeoN Geometry number (Strahler, 1958). Area/DD.

TCL Total channel length on OS 1:25 000 map (km).

MCL Main channel length. Length of the highest order stream in basin (Km).

NO1st Number of first order streams (Strahler, 1952)

NO2nd Number of second order streams.

NO3rd Number of 3rd order streams.

Rugg Ruggedness. Area/DD

SF Stream frequency (Horton, 1945). (2xNO1st-1)/Area

DI Drainage intensity (Faniran, 1968). SF/DD

BRt Bifurcation ratio (Horton, 1945). NO1st/NO2nd

Asp Aspect. ° deviation from North.

BWR Basin-water ratio. Ratio of drainage area to reservoir surface area at top water level.

Derived from Ordnance Survey, 1:50 000 maps.

(d) Reservoir morphometry

Resarea Reservoir surface area at top water level (km^2)

Resper Reservoir perimeter (km^2)

Derived from Ordnance Survey, 1:50 000 maps.

Age Years since reservoir operational

Orig cap Original reservoir capacity ($t.m^3$)

Curr cap Current reservoir capacity ($t.m^3$)

Cap loss Loss in reservoir capacity ($t.m^3$)

$Cap\ loss_{yr}$ Annual loss in capacity (m^3)

Area loss	loss per unit catchment area (m^3km^2yr)
$\%loss_{100yr}$	% capacity loss per century
Sed yield	Estimated sediment yield ($t.km^2yr$)
org yield	Estimated organic yield ($t.km^2yr$)

Source: Butcher,D. et al.,(1990) NB. This data only available for fourteen reservoirs.

(e) Land use

Moor	Catchment coverage by moorland (km^2)
Pasture	Catchment coverage by pasture (km^2)
Forest	Catchment coverage by forest (km^2)
%Moor	% Catchment coverage by moorland (km^2)
%Pasture	% Catchment coverage by pasture (km^2)
%Forest	% Catchment coverage by forest (km^2)

Source: Edwards,A.M.C. (1986).

(f) Local climate

$Rain_{month}$	Total monthly rainfall at each reservoir. (mm, mean 1986-88) Source: Yorkshire Water.
PE_{month}	Total monthly Potential evapotranspiration (mm, mean 1986-88)
SUN_{month}	Total monthly sunshine hours (mean 1986-88)
SMD_{month}	Monthly mean soil moisture deficit (mm, mean 1986-88)
$TEMP_{month}$	Mean monthly temperature (°C, mean 1986-88)
ANNPE	Mean annual Potential evapotranspiration (mm, mean 1986-88)
ANNSUN	Mean annual sunshine hours (mean 1986-88)

ANNSMD	Mean annual soil moisture deficit (mm, mean 1986-88)
ANNTEMP	Mean annual temperature (°C, mean 1986-88)

Source: Meteorological office, MORECS bulletins 1986-88.

3.2.2 Results and discussion

The variation in water quality found between the selected reservoirs was analysed by correlation and stepwise regression techniques. All significant correlations between water quality variables and catchment variables are shown in table 3.3.

The variation in the mean true colour between reservoirs is significantly correlated with only two independent variables. These are the %Moor (% catchment coverage by moorland), and %1011b (% coverage by the Winter hill soil series). For the mean apparent colour, %1011b is the only significant correlation.

Measures of variation in colour are important in identifying those characteristics that make catchments prone to periods of unusually high colour. The variables describing true colour variation (Standard deviation, maximum, minimum, range, 'high colour') are correlated with up to six independent variables. The most significant of these are, again, %Moor, and %1011b. For apparent colour, the only significant independent variable is %1011b. 'High colour', the variable that best describes periods of above average colour, is correlated with just one independent

variable, %1011b.

Average reservoir colour, and colour variability are both strongly correlated with the same catchment characteristics. This indicates that those characteristics responsible for colour also tend to make a catchment prone to above average intensity colour flushes. These characteristics %Moor and %1011b describe the extent of peat moorland. However, %Moor may only be a significant factor due to its autocorrelation with %1011b ($r=0.6301$, $N=43$, $P<0.001$), which has the highest single correlation with the colour variables. Thus the greatest influence on the spatial distribution of discoloured water is the spatial distribution of winter hill peat.

Table 3.3. Significant Pearson correlations between colour variables and catchment characteristics.

(a) True colour, N=25

Catchment characteristic	Mean	Std. Devn.	Max.	Range	High colour
%1011b	0.5337	**0.5984**	0.5265	0.4928	0.5546
%Moor	0.4700	-	**0.6077**	**0.6322**	-
Cren	-	-	0.5110	0.5206	-
TCL	-	-	0.4903	0.5047	-
Res per	-	-	0.5649	0.5877	-
per	-	-	0.4967	0.5176	-
area	-	-	0.5455	0.5697	-

(b) Apparent colour, N=46

%1011b	**0.4828**	0.4223	0.4118	0.4728	0.4928

(c) Water pH, N=25

	Min pH	Mean pH	Max pH
North	**0.6512**	**0.5749**	-
Min_{Elev}	-0.5489	-0.5379	-
ANNPE	-0.5255	-0.4731	-
ANNTEMP	-0.4930	-0.4663	-
	P< 0.01	P< **0.001**	

Apparent colour and water pH were correlated (r=-0.4408, N=27, P<0.05). True colour was not correlated with pH and this is partly attributed to the smaller sample size. The direction of the apparent colour correlation indicates that coloured waters tend to be acidic. This is consistent with the inclusion of organic acids in the structure of colour causing compounds.

Mean water pH was correlated with four catchment characteristics. Correlation with Minimum pH were marginally higher, while no correlation exists with Maximum pH. This suggests that these four catchment characteristics are associated with acidity, not pH.

The waters of the reservoirs are significantly more acid towards the South of the study area. This does not relate directly to the distribution of peat moor, and may be the result of differential acid deposition. The most acidic waters are found in the southern Pennines, around Sheffield

and Manchester, and may reflect the historic pattern of SO_2 deposition is Northern England.

Reservoir pH decreases significantly as catchment height, mean annual temperature and potential evapotranspiration increase. These factors may act to promote acidity in two ways. Higher temperature and potential evapotranspiration may promote soil decomposition and therefore the production of water soluble organic acids. Secondly, higher reservoirs have catchments with a greater proportions of organic soils, and therefore more organic acids. Minimum catchment height is strongly correlated with %1011b ($r=0.7140$, $N=43$, $P<0.001$). Waters from higher catchments, with peat soils of low mineral content and therefore a lower buffering capacity, are therefore prone to acidification.

Water quality parameters were further related to catchment characteristics by using stepwise multiple regression. A requirement of regression analysis is that the dependent variable be normally distributed. Transformations were performed where appropriate (table 3.4).

Results of the regression analysis are presented in table 3.5. For both true and apparent colour, mean reservoir colour is best explained by variables describing the distribution of organic soils and rainfall. The %1011b is the most significant factor in both cases, but accounts for less than a third of total colour variation. The moorland variable is not entered into either colour regression, and again, demonstrates its autocorrelation with %1011b

(r=0.6301, N=43, P<0.001). For both true and apparent colour the next most significant variable is a rainfall variable. Rainfall is secondary only to the areal extent of deep peat in accounting for the spatial distribution of colour. That is, rainfall is essential to the continued solubilisation and movement of organic matter.

Table 3.4 Goodness of fit of dependent variable (colour, pH) to normal distribution.

Dependent variable	Transformation	After transformation Kurtosis	Skewness
True colour:			
Mean	Square root	-0.75	-0.06
Standard deviation	Square root	-1.08	-0.14
Maximum	Square root	0.38	0.40
Minimum	Log 10	1.33	1.36
Range	Square root	0.65	0.21
High colour	Square root	-0.75	-0.01
standard error		0.46	0.90
Apparent colour:			
Mean	Log 10	1.19	-0.35
Standard deviation	Log 10	2.36	1.12
Maximum	Log 10	1.38	1.07
Minimum	Log 10	-0.28	-0.27
Range	Log 10	5.90	-1.03
standard error		0.73	0.37

Water pH:

Mean	Square root	-0.92	-0.63
Maximum	None	-0.11	-0.09
Minimum	Log 10	-0.84	-0.61
standard error		0.87	0.45

Colour is related to total rainfall in July (True) and March (Apparent). This is later than the 'autumn flush' recognised for many upland catchments, and may be attributed to the average residence time of water in the reservoirs, although in some cases these are known to be very short (McDonald et al., 1990). Alternatively this may be a reflection on the quality of the colour database. The assumption of an even temporal distribution of colour data may be false. The more extensive apparent colour database indicates that March rainfall is most significant and this may be indicative of the relatively dry winters experienced during 1986-88. Figure 3.2 shows that the second greatest increase in average monthly rainfall during the study period was from February to March, which would contribute significantly to a March colour flush.

The areal extent of the Belmont soil association (%651a) is a further significant factor controlling the variation in true colour. Like the Winter Hill association (1011b), the Belmont association consists of raw acidic peat, and therefore acts as an additional organic matter source. The level of explained variance is less than that for Winter hill. This is attributed to the depth of peat; Winter Hill peat is described by the soil survey as 'thick', the

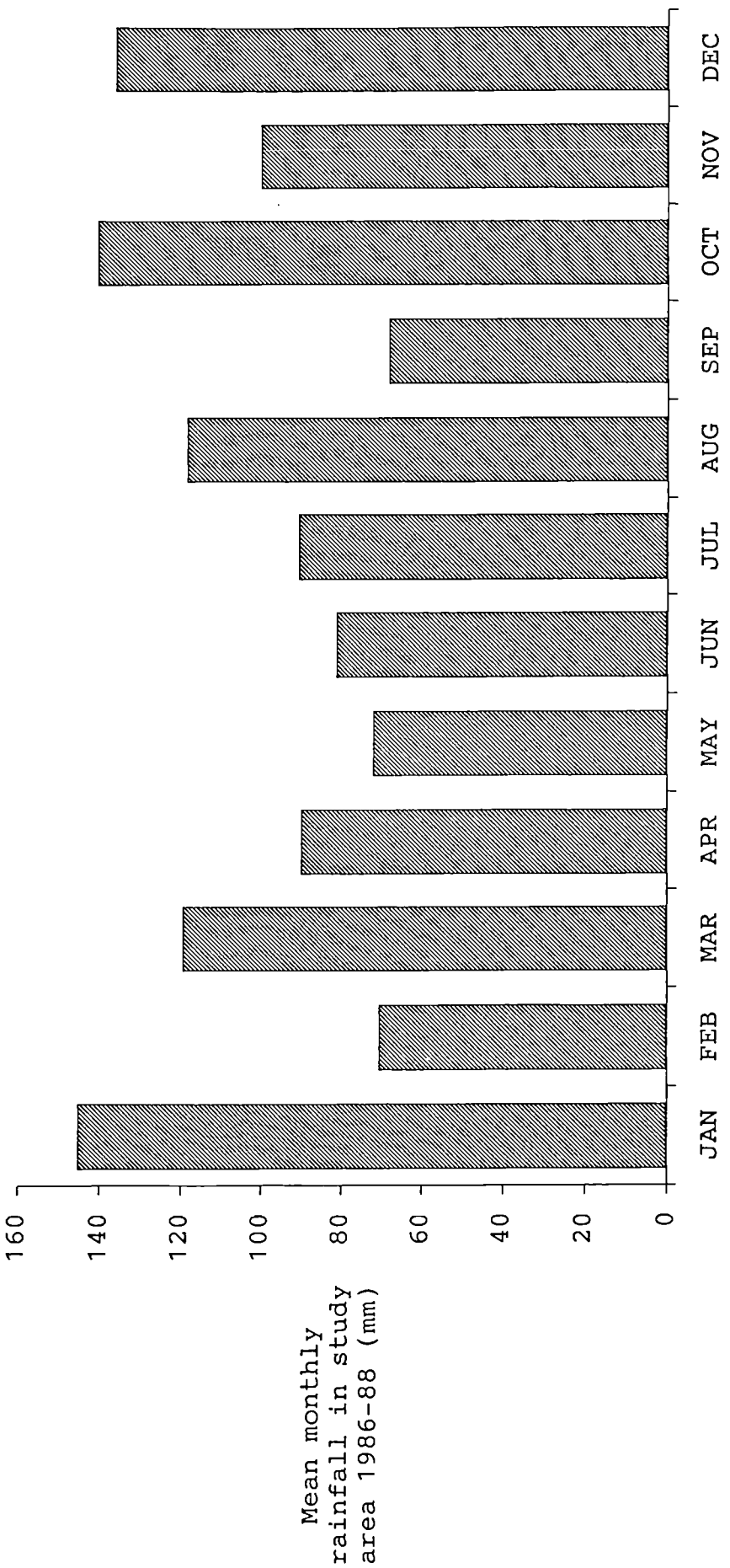


Figure 3.2 Mean monthly rainfall for all reservoirs in regional analysis of colour distribution, 1986-1988

Belmont peats as 'thin'. Both the spatial distribution and depth of peat are influential in determining the spatial distribution of colour. This suggests that the volume of peat in a catchment strongly determines the degree of runoff discoloration.

The variation in true and apparent colour experienced by each reservoir was accounted for by a range of independent variables. However, three were recurrent. Two of these, %1011b and rainfall were significant in accounting for both colour variation and mean reservoir colour. This supports the conclusion drawn from the correlation matrices above. That is, those factors responsible for high colour are the same factors that make a catchment prone to above average intensity colour flushes. However a third factor also significantly affects the colour variability. This is the intensity of the catchments' drainage network. Drainage intensity is positively correlated with colour. This indicates that, following rainfall, peat covered catchments with high drainage intensities are more prone to periods of high colour release, than similar catchments with poor drainage. An intense drainage network may promote high colour flushes in two ways. A well drained catchment may have a marginally lower water table, which in deep peat would result in a significantly greater zone of aerobic decomposition, and so a larger colour source area. Secondly, a high drainage intensity allows more rapid movement of drainage water, and therefore faster export of organic solutes.

Table 3.5 Regression of colour and pH variables on catchment characteristics and local climate.

(a) True colour

Dependent	Independent	r^2	SE	P ANOVA
Mean	%1011b	0.26690	0.27839	0.0082
	$Rain_{July}$	0.44329	0.24805	0.0016
	%651a	0.59921	0.21542	0.0002
	Forest	0.69903	0.19444	0.0001
Std.Devn	%1011b	0.37187	0.24331	0.0012
	DI	0.53540	0.21396	0.0002
	$Rain_{March}$	0.68552	0.18017	0.0001
	82 (LWP)	0.75834	0.16184	0.0001
Minimum	none	-	-	-
Maximum	%1011b	0.29267	0.63944	0.0052
	DI	0.41007	0.59709	0.0030
	Cren	0.57064	0.51809	0.0004
	$Rain_{July}$	0.66679	0.47065	0.0001
Range	Moor	0.28069	0.61355	0.0065
	Forest	0.42110	0.57930	0.0024
	%1011b	0.52366	0.53785	0.0012
	$Rain_{March}$	0.62237	0.49071	0.0004
	DI	0.71869	0.43453	0.0001

High colour	%1011b	0.30655	0.52798	0.0041
	DI	0.45976	0.47649	0.0011
	$Rain_{March}$	0.61263	0.41298	0.0001
	Forest	0.70525	0.36913	0.0001
	$Rain_{Jan}$	0.78030	0.32697	0.0001

(b) Apparent colour

Dependent	Independent	r^2	SE	P ANOVA
Mean	%1011b	0.27261	0.25556	0.0005
	$Rain_{March}$	0.38167	0.23879	0.0001
	BWR	0.46856	0.22443	0.0001
Std.Devn	%1011b	0.28663	0.25843	0.0004
Minimum	%1011b	0.24837	0.41181	0.0011
	SMD_{Feb}	0.33480	0.39261	0.0005
Maximum	%1011b	0.19786	0.26136	0.0040
	$Rain_{Nov}$	0.31813	0.24421	0.0008
Range	none			

(c) Water pH

Dependent	Independent	r^2	SE	P ANOVA
Minimum	North	0.41744	0.69360	0.0003
	DI	0.51846	0.64360	0.0002
	Min_{Elev}	0.66191	0.05509	0.0001
	SMD_{Nov}	0.79542	0.04382	0.0001

Mean	North	0.33150	0.19129	0.0017
	%1011b	0.47594	0.17286	0.0004
	ANNPE	0.63120	0.14813	0.0001
	DI	0.74716	0.12541	0.0001
	Elgn	0.83181	0.11074	0.0001
	80 (lime)	0.91581	0.07787	0.0001
	%711p	0.94652	0.06376	0.0001
	$Rain_{Nov}$	0.96389	0.05392	0.0001
	Aspect	0.97242	0.04857	0.0001
Maximum	Min_{Elev}	0.18521	1.05456	0.0250
	%713g	0.36379	0.95108	0.0044
	%541o	0.52388	0.84046	0.0006

Variations in both mean and minimum water pH are best accounted for by reservoir latitude, a possible reflection of historic patterns of acid deposition. Mean water pH and %1011b are not significantly correlated. However, once latitude is entered into the regression, %1011b accounts for the greatest single portion of variability in mean water pH. Winter Hill peat has an average pH ≤4, and will act as a source of organic acids, which not only colours the water, but lowers its pH. Minimum pH is accounted for by reservoir latitude and drainage intensity. Drainage intensity is negatively correlated with Minimum pH, and is significant in determining maximum and 'High' colour. This suggests that periods of high colour and acidic flushes are products of similar catchment characteristics and processes.

3.2.3 Conclusion

The spatial distribution of discoloured water in Yorkshire is largely determined by the distribution of organic rich soils and rainfall. The Winter Hill soil association is the most dominant factor in determining colour distribution. This soil association comprises very acid, perenially wet peat to a depth of at least 40 cm, and is the main source area for dissolved organic matter. The Belmont association, with its' thin peat surface, acts as a secondary source.

The distribution of peat soils are dominant in determining the distribution of discoloured water. Rainfall is the next most significant factor in determining this distribution. Organics are removed from peat catchments as colour by the movement of water. It is not clear which months rainfall is most significant, due to unknown reservoir storage periods and a possible uneven temporal distribution of colour data. However, periods of high colour appear to follow increases in rainfall.

In addition to peat and rainfall distribution, drainage intensity has a significant impact on the distribution of colour. Intense drainage networks may promote high colour flushes by lowering the water table, producing a greater zone of aerobic decomposition and so a larger colour source area. A high drainage intensity also allows more rapid movement of drainage water, and therefore faster export of organic solutes.

Water colour and pH were found to be associated; highly

coloured waters tend to be very acidic, and vice versa. Acid waters are associated with peat deposits and drainage intensity. This indicates that acid waters are poduced as a result of processes similar to those that produce colour, and is further evidence that water is coloured by organic acids. However, the most significant factor determining water pH was the latitude of the reservoir. Reservoirs at the southern extent of the study area around Leeds, Bradford, Sheffield and Manchester were found to be more acidic than those further north in the Yorkshire Dales and North York moors. This may be attributed to past differences in the deposition rates of sulphur dioxide and nitrous oxides.

In this analysis the level of explained variance for mean colour is 70% for true colour, and only 46% for apparent colour. The deficiencies in the level of explained variance may partly be attributed to the quality of the data. Colour data was derived from measurements taken downstream of the reservoir. These colour measurements therefore include the effects of water residence times in the reservoir, and possible mixing of waters from other sources. The temporal distribution of sampling may not be even, making the determination of possible associations with climatic variation difficult. It is likely that water sampling is more frequent during periods of high colour. With the exception of rainfall data, all climate data relates not to the individual reservoir catchment, but to the 40 x 40 Km

square in which the reservoir lies. Only six of these MORECS squares cover the study area. This is the best climate data available, but may not be at sufficient resolution for the purpose of this analysis. Basin morphometric and soils variables were determined from OS 1:50 000 and soil survey 1:250 000 maps respectively. Data determination from these maps allows for a relatively large margin for error.

Analysis of the spatial distribution of colour at a subcatchment scale allows many of these problems to be overcome. Water samples can be collected immediately before the reservoir. It can be assumed that all sub-catchments experience the same climate, allowing climatic and temporal variation to be excluded. Basin morphometry and soils data, collected at 1:25 000 will have a greater degree of accuracy. Finally local knowledge of the catchwater may assist in the identification of factors, important to water discolouration, that have not previously been included in the analysis. An analysis of the spatial distribution of colour at the sub-catchment scale is detailed below.

3.3 The spatial distribution of coloured water within a single catchwater system

3.3.1 Initial catchwater studies

The spatial distribution of coloured water within two major Yorkshire catchments, the Upper Nidd (SE 06 77) and Washburn valley (SE 16 56), was investigated. The colour distribution within these drainage basins was determined by

spot sampling of first order streams in the Upper Nidd valley, and second order streams in the Washburn valley. The areas drained by these streams are hereinafter termed 'sub-catchments'.

These water colour surveys demonstrate that apparently similar sub-catchments, often adjacent to each other, produce marked differences in runoff colour. For both basins consistent differences in water colour between sub-catchments were observed (table 3.6). This significant observation has permitted the development of catchwater management strategies designed to reduce the colour of water arriving at treatment works (McDonald et al., 1987;McDonald and Naden, 1987).

The consistently high water colours were found to originate from sub-catchments with organic rich, and particularly peat soils. Observations in the Upper Nidd indicate that sub-catchments with predominantly South facing slopes and those subject to moorland burning or ditching tend to produce runoff of a consistently high colour. A full account of the Upper Nidderdale and Washburn valley work can be found in McDonald et al., (1990).

Table 3.6 Water colour variations in the Upper Nidd and Washburn valleys, North Yorkshire.

Upper Nidd Valley				Washburn valley			
Sub-catchment	Colour (au m^{-1}) Mean	δ	N	Sub-catchment	Colour (au m^{-1}) Mean	δ	N
HS2	10.37	4.39	23	F1	2.72	1.47	26
HS3	2.67	1.84	23	F2	3.48	1.74	26
HS4	4.92	2.14	23	F3	6.60	3.14	26
HS5	5.72	5.52	22	T1	4.10	1.90	26
HS6	3.77	3.30	20	T2	7.76	2.91	26
HS7	6.46	2.97	21	RGA	5.95	1.90	15
HS8	6.99	6.98	21	RGB	5.76	1.94	16
HS9	7.64	6.15	21	RGC	4.18	2.91	21
HS10	6.79	3.18	21	RGD	4.31	2.89	16
HS11	7.15	3.14	21	RGE	5.99	2.35	16
HS12	4.45	2.02	21	RGF	5.98	2.29	16
HS13	3.72	1.87	21				
HS14	11.59	5.69	20				
HS15	4.75	2.78	21				
HS16	4.17	2.47	20				

3.3.2 Characterisation of non-point colour sources in the upper Burn valley, North Yorkshire

3.3.2.1 Introduction and methods

In this section the spatial distribution of discoloured water within, the upper Burn valley, North Yorkshire (SE 17 80) is determined. The observed distribution is related to

a detailed characterisation of forty six sub-catchments within the basin. Sub-catchments are characterised in terms of their morphology and pedology. Colour is also related to a range of other water quality parameters.

(a) The study area

The study area (figure 3.3) containing Roundhill and Leighton reservoirs is situated in the headwaters of the river Burn, a tributary of the river Ure, N.Yorkshire, UK and covers an area of approximately 60km^2. The reservoirs were built by the then Leeds corporation waterworks to supply Leeds from Leighton reservoir, and the Claro water board supplying Harrogate from Roundhill reservoir. The source of the river Burn is located in an adjacent valley, Colsterdale, which provides a third catchwater. Water from this area is abstracted from the river Burn, Birk Gill and Spruce Gill beck, where it flows under gravity to Leighton reservoir.

These catchments range from 200 to 500 m and are largely covered by rocks of the Millstone grit series. There are also areas of sandstone, shale, mudstone, limestone and in the upper reaches of colsterdale, thin seams of coal. The land use of this area is mixed, with areas of grouse moor grazed by sheep, reclaimed grassland, some lowland arable land and mixed woodland managed by the Swinton estate.

(b) Water quality variables

Throughout 1989 waters from 45 of the most

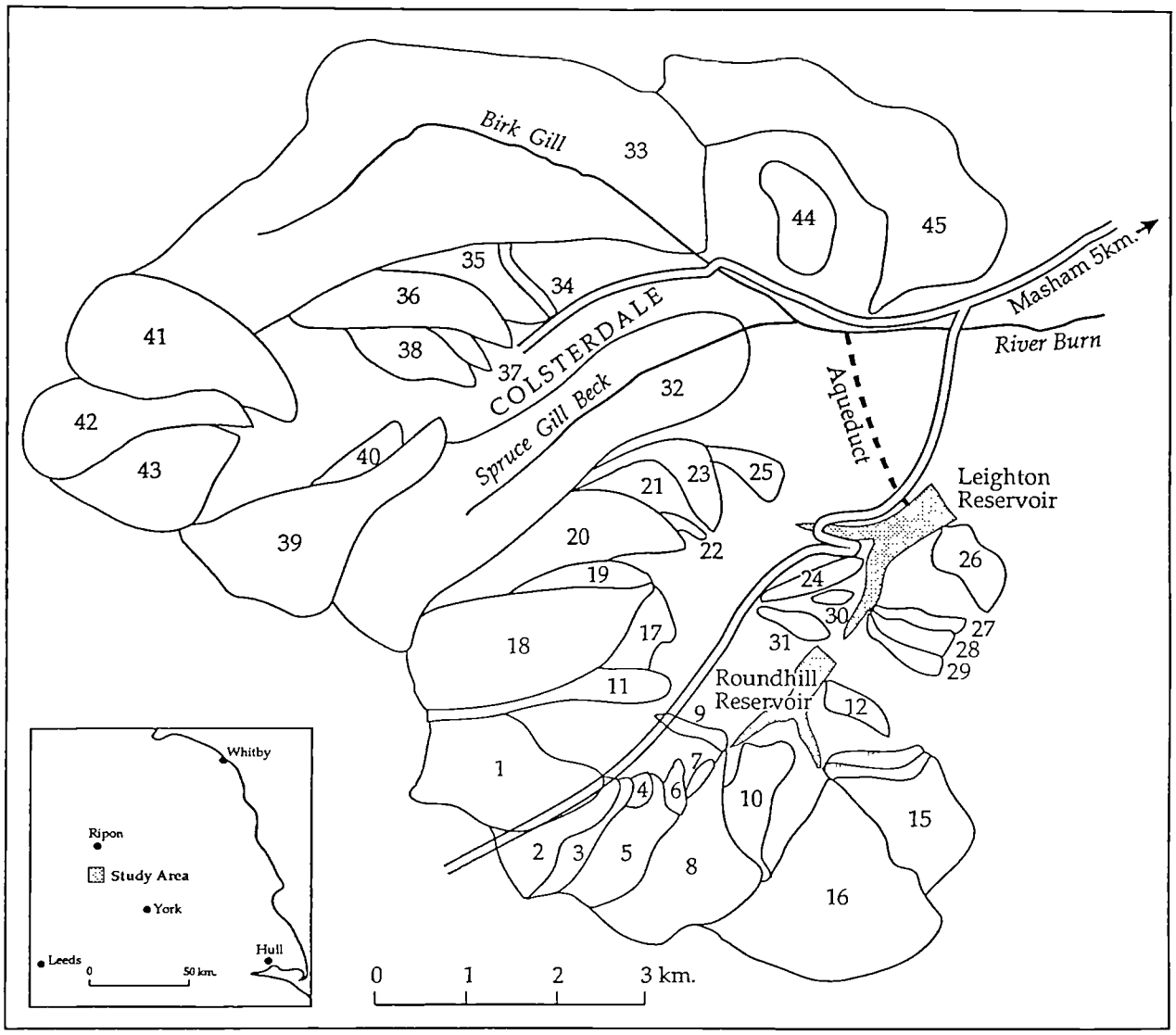


Figure 3.3 Upper burn study area

significant sub-catchments, in terms of discharge, were sampled (figure 3.3). In all, fourteen 'snapshots' were taken, with more frequent sampling during the wetter autumn and winter periods when greater discoloration is experienced.

Each sample was analysed for colour and a further thirteen determinands. True colour was measured after 0.45μ filtration on a Pye unicam UV/Vis spectrophotometer at $400nm^{-1}$. Several other water quality parameters thought to be associated with colour were also determined. Conductivity and pH were measured within eight hours of collection, pH with a low conductivity probe. aluminium, manganese, iron, calcium and magnesium were measured by atomic absorbtion spectrophotometry. Maximum deviation of standards from linearity was ≤ 2% (except aluminium, ≤ 7%). Flouride, chloride, nitrate, phosphate and sulphate were measured on a Dionex 4000i ion chromatograph (maximum deviation of standards from linearity ≤ 1%). Total hardness was obtained by calculation. Analytical operating conditions are detailed in appendix II.

Fluctuations in water quality during the sampling period were assessed by sampling sub-catchment 'one' at the beginning and end of the eight hour sampling period. Maximum deviations (table 3.7) were found during October and February-March, when rainfall was greatest, but were largely within the band of experimental error. Two tailed t-tests demonstrate that no significant differences exist between the two sets of samples. Thus each sample group can

be considered a true snapshot.

Table 3.7. Deviation in chemical concentrations of sub-catchment one during sampling period.

	Difference			t	2 tail	date of max
	Mean	Max	δ		prob	difference
Colour	0.2980	0.585	0.2154	1.22	0.256	29-Oct
pH	0.1670	1.130	0.3624	0.77	0.463	15-Oct
Cond	8.8000	49.000	15.2707	0.08	0.937	4-Feb
Al	0.0250	0.090	0.0288	-1.57	0.156	29-Oct
Mn	0.0140	0.047	0.0181	-1.39	0.203	29-Oct
Fe	0.0390	0.138	0.0420	-2.28	0.052	29-Oct
Ca	0.6500	1.960	0.6970	1.78	0.113	15-Oct
Mg	0.2340	0.600	0.1965	1.25	0.246	29-Oct
Tothard	2.2140	6.701	2.4900	2.44	0.041*	15-Oct
F	0.0310	0.240	0.0756	1.21	0.261	15-Oct
Cl	3.6430	21.170	6.8670	-0.83	0.431	4-Feb
No_2	0.3381	1.348	0.4625	-0.91	0.390	12-Mar
H_3po_4	0.0679	0.611	0.2038	1.00	0.347	15-Oct
So_4	4.0925	25.122	7.9973	-0.26	0.798	19-Feb

(All units ppm except; pH, colour (au m^{-1} at 400nm), Total Hardness (mg l^{-1} $CaC0_3$ equivalent) and conductivity (μs). * P <0.05, Total hardness determined by calculation.

(c) Catchment morphometric characteristics

For each subcatchment sampled in the Upper Burn

catchwaters, thirty two morphometric variables were calculated. These variables include those detailed in table 3.2 (c) above, with several additions. The additional variables describe the areal extent of particularly flat catchment areas, and the degree to which they are incised by natural drainage (table 3.8). These variables are included as field observations indicated that such areas may be significant sources of colour (section 3.4.1). All values were determined from 1:25 000 scale maps, and where appropriate, a digitising tablet was used. At this scale the number of springs and catchment main stream slopes can also be determined.

Table 3.8. Description of Morphometric variables additional to those presented in table 3.2 (c).

$CLA_{5°}$	Channel length in area of slope ≤5°.
$\%TCLA_{5°}$	Percent of TCL in ≤5°.
$CLA_{3°}$	Channel length in area slope ≤3.
$\%TCLA_{3°}$	Percent of TCL in ≤3°.
$A_{5°}$	Area (Km^2) with a slope of ≤5 degrees.
$\%A_{5°}$	($A_{5°}$/area) x 100.
$A_{3°}$	Area (Km^2) with a slope of ≤3 degrees.
$\%A_{3°}$	($A_{3°}$/area) x 100.
Spr	Number of springs depicted on OS 1:25 000 map
MSS	Main stream slope (Newson, 1975). Slope between 10 and 85 % of main stream length.
	Derived from OS 1:25 000 maps.

(d) Catchment soil characteristics

The soils in the study area are diverse, including twelve soil associations. These include the Revidge (311a), Rivington (541g), Belmont (651a), Maw (652), Dunkeswick (711p), Hallsworth (712d), Brickfield (713g), Ticknall (713h), Kielder (721a), Roddlesworth (721b), Wilcocks (721c), and Winter hill (1011b) associations (sub group shown in parenthesis). These soils range from loam and clay soils to blanket peat. The best published soils data for this area is at a scale of 1:250 000, which is of limited value for this study. Therefore a soils map at 1:25 000 scale was prepared by the Soil Survey and Land Use Centre. This map represents the most detailed soil information available for this area. However, errors may exist as it was compiled from air photo interpretation with less ground testing than is usual for published maps.

3.3.2.2 Results and discussion

(a) The seasonal pattern of colour

The annual pattern of colour flow in the three main catchwaters and rainfall for the whole catchwater is presented in figure 3.4. High colour flows were experienced during February, March and October. These were the wettest periods in a drier than average year, with only 91.9 % of the long term average rainfall. Periods of high colour came in months where the average monthly rainfall was high following a previous dry month (January to February 31.5-

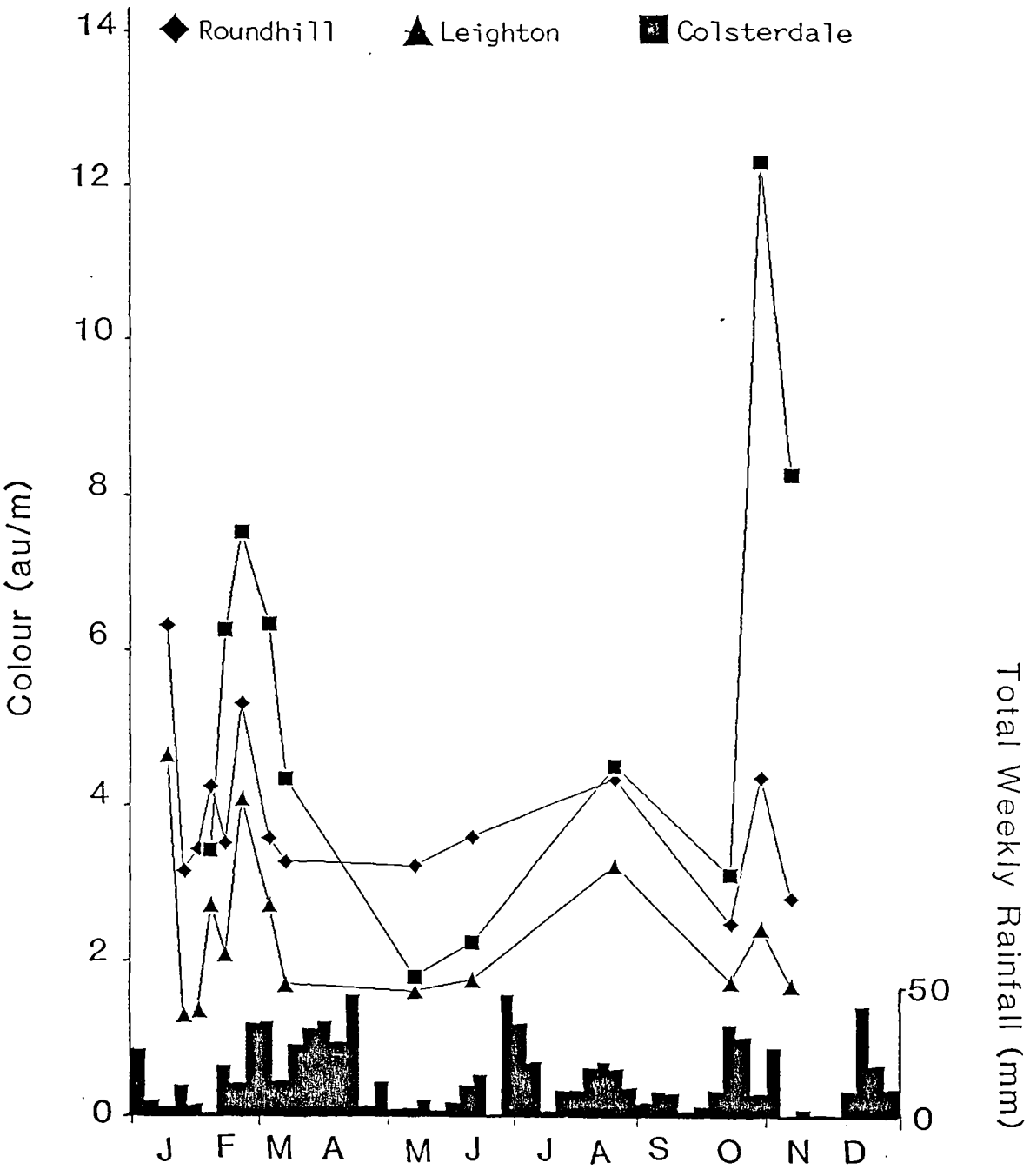


Figure 3.4 Colour levels in the three major catchwaters of the upper burn valley, 1989

117.5 mm, September to October 17.4-101.9 mm). The timing of these high colour flows is consistent with that observed in many other catchments, including the Upper Nidd and Elan valleys, where high colour flows follow high rainfall, and 'flushing' of dissolved organic matter. The seasonal pattern of colour flow in these catchments can thus be considered typical.

(b) The spatial distribution of colour

The spatial variation in colour is presented in figure 3.5. Consistent differences in colour between sub-catchments are evident throughout the catchwater system. The colour of runoff from some sub-catchments, particularly from those in Colsterdale, is consistently higher than from others. This is a significant observation as it supports previous conclusions drawn from the Upper Nidd and Elan valley studies (McDonald et al., 1990; Boon et al., 1988). This implies that catchwater management strategies designed to reduce the colour of water arriving at treatment works are likely to be effective when applied on a wider geographical scale.

(c) Colour and catchment characteristics

Of the forty four variables used to describe the catchments sampled in the catchwater system, only two were significantly correlated with runoff colour. These were %1011b ($r=0.4363$, $N=48$, $P<0.001$) and the per cent of total channel length found in areas of catchment with slopes $\leq 5°$ degrees, $\%TCLA_{5°}$ ($r=0.3833$, $N=48$, $P<0.01$). The Winter hill

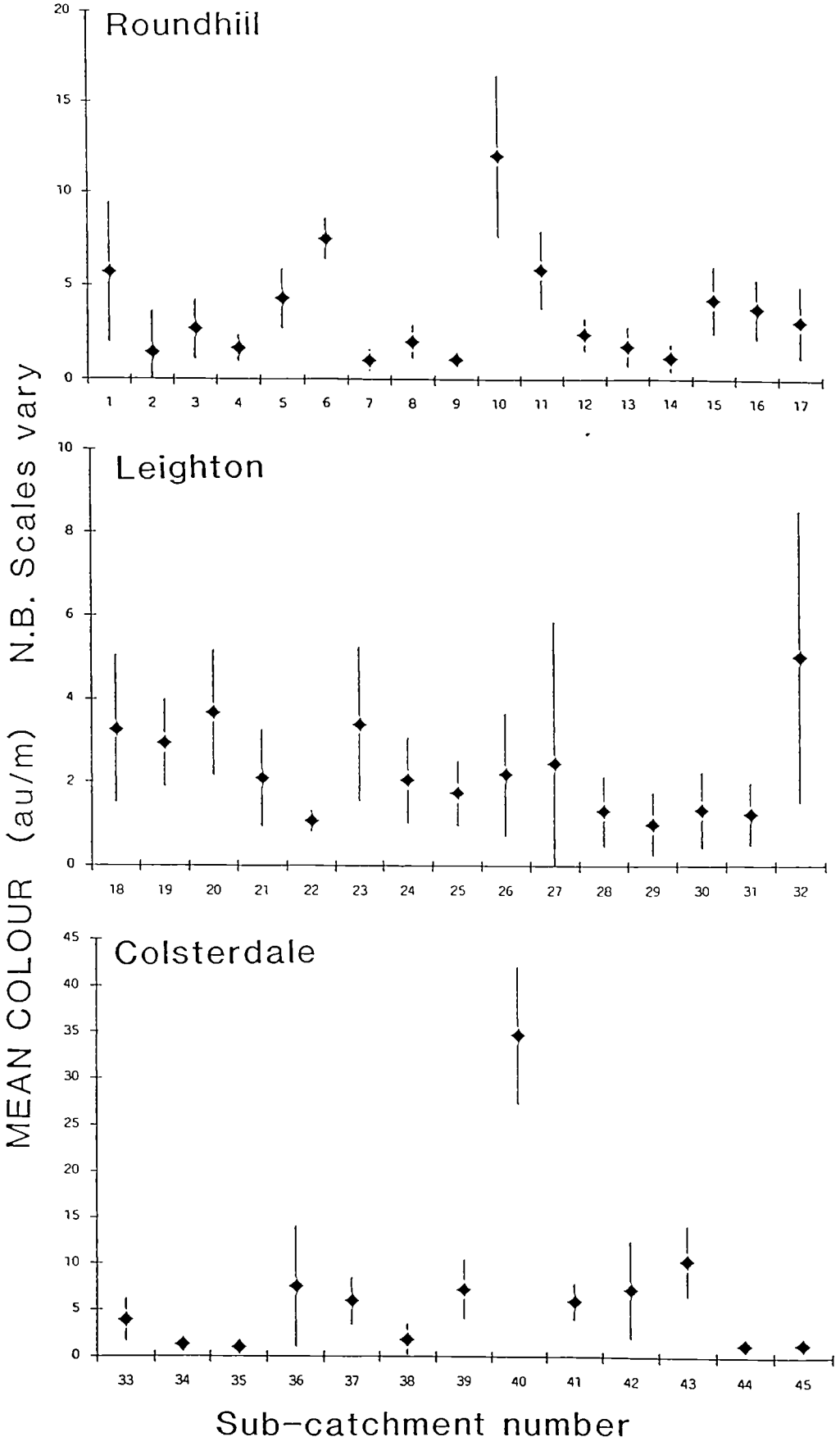


Figure 3.5 Upper burn catchment colour variation

association is very acid blanket peat to a minimum depth of 40 cm. It is the deepest organic soil in the Soil Survey classification and has the greatest volume of organic material in the catchwater. Thus assuming that colour is imparted to water by dissolved organic material, the Winter hill peat represents the main source of discolouring material in the basin. This observation is consistent with the regional analysis, which also concluded that the distribution of the Winter Hill soil association is the most dominant factor in determining the spatial distribution of colour.

Colour was also positively correlated with $\%TCLA_{5^{\circ}}$. Plateau areas have low hydraulic conductivities, giving water the maximum potential to dissolve decomposition products and become coloured. Combination with a high drainage density promotes discoloration in two further ways. A well drained catchment will have a lower potentiometric surface, a larger aerobic decomposition zone and therefore a larger pool of organic, water discolouring material. A high drainage density will also allow more rapid movement of drainage water, a faster export of organic solutes and therefore a more intense colour flush.

3.3.2.3 Regression model

The data collected from the survey of the Upper Burn can be used to estimate the discolouration of water from catchments where no water sampling has taken place. This can be done by producing a predictive equation in a similar

manner to that done for flood prediction from ungauged catchments (NERC, 1975).

Water colour was related to catchment morphometric and soils data using a stepwise multiple regression technique. The dependent variable, colour, approximated to a normally distributed curve after a $\log_{10}$ transformation (Kurtosis = 0.21, Skewness = 0.64). The resulting equation is:-

$$\text{Log}_{10}\text{Colour} = 0.0051(\%TCLA_{5^\circ}) - 0.6090(MSS) + 0.0036(\%1011b) + 0.214$$

With all catchments entered into the equation, 60.1% of the variance can be explained by three independent variables ($P<0.001$, $N=45$). These variables include the extent of Winter Hill peat, and the extent of dissected 5° plateaus. A third component, Main stream slope (MSS) is significant when entered in the regression model, although not significantly correlated with colour. The negative direction of the relationship is a further indication that shallow slopes promote water discoloration. The final, highly significant, predictive model demonstrates the rôle highly dissected peat plateaus play in determining the spatial distribution of discoloured runoff within the catchwater.

The predictive power of the equation is further improved to 81.6% ($P<0.001$, $N=42$) by dropping three catchments from the analysis whose standardised residual exceeds +1.5. These catchments were dropped from the analysis as field

observations suggested that two significant factors had not been included in the original analysis. Two of the catchments (b slee, ATGG) were extensively and intensively burnt for grouse moor management, while the third has an intense artificial ditch network that is not fully represented on the OS 1:25 000 map. The residual analysis thus points to further significant influences on water discoloration processes. It is assumed that artificial ditching promotes discolouration in the same manner as natural drainage, through elevated decomposition and organic solute transport, but its high intensity may result in a greater severity of discolouration. The process by which moorland burning contributes to discoloration is uncertain. Colour may result from rapid decomposition of surface peat, from water table lowering and more prolonged decomposition of sub-surface organic matter, or from a combination of these processes. However, it is apparent that upland land management practices can have a major impact on discoloration.

3.3.2.4 Relationship between colour and other water quality variables

Determination of the relationships between colour and other water quality parameters is thought to aid understanding of colour production processes and origins. The complexation of dissolved organic matter, including humic and fulvic fractions, following ionic exchange has been observed for both cationic and anionic species. Humic substances may be complexed with iron (eg Shapiro, 1964; Christman and

Ghassemi, 1968; Tipping, 1981; Pennanen and Frisk, 1984), manganese (Takkar, 1969) and other trace metals (Gibbs, 1973; Saar and Weber, 1982), while anionic complexation has been observed for phosphate (Koenings and Hooper, 1976) and nitrate (Fuchsman, 1980). Heikkinen (1991) has observed a strong positive relationship between iron and colour (Absorbance at 420 nm after 0.7μm filtration) for the Kiiminkijoki river in northern Finland.

The correlation matrix (table 3.9) of all water quality variables in the study shows significant relationships between colour and iron, and colour and aluminium ($P<0.001$). A significant negative correlation ($P<0.001$) also exists between pH and colour, which is consistent with rôle of organic acids in discolouring water. There are also strong negative correlations between pH and iron, aluminium and manganese. This suggests that iron, aluminium and manganese either share a common source with acidic coloured water, or are complexed with it. No other species were directly correlated with colour.

Table 3.9. All water quality variables correlation matrix.

	Colour	pH	Cond	Al	Fe	Mn	Ca
pH	**-.5130**						
Cond	.1346	**.3763**					
Al	**.6132**	**-.7507**	.1301				
Fe	**.8456**	**-.5925**	-.0391	**.5660**			
Mn	.1234	**-.6157**	-.2459	**.4908**	.3263		
Ca	-.2203	**.6836**	**.8240**	-.2204	-.2878	**-.3399**	
Mg	-.2502	**.6781**	**.7985**	-.2911	-.2902	**-.3826**	**.8203**
Fl	-.0677	.1695	.1280	-.0648	-.0535	-.1237	.2092
Cl	-.2634	**.3625**	**.5550**	-.1672	-.3009	-.2504	**.4078**
NO_2	-.1318	.2203	**.3389**	.0264	-.2742	-.1890	.3205
H_3PO_4	-.0950	.0759	.0758	-.1184	-.1248	-.1269	.1047
SO_2	.0880	.3089	**.7180**	-.0184	-.0957	-.0246	**.6218**
TotH	-.1869	**.6498**	**.8479**	-.1803	-.2448	-.3331	**.9436**

	Mg	Fl	Cl	NO_2	H_3PO_4	SO_2
Fl	.1944					
Cl	.5988	.2590				
NO_2	.2463	.2588	.3390			
H_3PO_4	.1078	.0434	.2440	.0539		
SO_2	.6578	-.0032	.3909	-.0662	.1316	
TotH	.9167	.1720	.4535	.3029	.1152	.6578

N=658 P < 0.01 P < 0.001

Iron, aluminium, manganese and pH were correlated with catchment soil and morphometric characteristics. Those characteristics with significant correlations are presented in table 3.10. The variable %1011b is common to both colour and iron, while $\%TCLA_{o5}$ is common to colour, iron and aluminium. This suggests that aluminium, and in particular iron, have a common source of origin with colour.

Table 3.10. Significant Pearson correlations (r) between selected water quality variables (annual means) and subcatchment characteristics.

Catchment characteristic	Colour	pH	Mn	Al	Fe
Max_{elev}	0.2031	-0.3220	0.2198	0.1994	0.3381
Min_{elev}	0.3257	-0.3724	0.1539	0.2576	0.4127
Spr	-0.1864	0.3490	-0.1591	-0.0820	-0.2656
$TCLA_{5o}$	0.1861	-0.2431	0.1620	0.1327	0.4169
$\%TCLA_{5o}$	0.3833	-0.3340	0.2687	0.4890	0.5410
$\%TCLA_{3o}$	0.2278	-0.2316	0.1794	-0.3702	0.4134
%1011b	0.4363	-0.3917	0.2200	0.2505	0.5480
N=48	P < 0.01		P < 0.001		

Regression models were able to account for 68.5, 42.6 and 25.1 per cent of the variance in iron, aluminium, and manganese respectively. The variable $\%TCLA_{5^\circ}$ was common to all regression models (table 3.11), and was accompanied by independent variables describing catchment slope and extent of organic soil. Further analysis identified a total of six sub-catchments with residual values in excess of 1.5. Of these six sub-catchments, three were common to all models, including that for colour. This suggests that burning and ditching practices may be significant not only in terms of colour production, but in terms of the level of iron, aluminium and manganese in runoff draining such catchments.

Table 3.11 Regression models for dissolved metals in the Upper Burn valley, North Yorkshire.

$$Log(Fe) = 0.0086(\%TCLA_{5^\circ})-0.8993(MSS)+0.0049(\%1011b)+0.0070(\%652)-1.401$$

$$Log(Al) = 0.0034(\%TCLA_{5^\circ})-10.0019(RR)-0.653$$

$$Log(Mn) = 0.0053(\%TCLA_{5^\circ})-0.0117(\%712d)-1.213$$

The broad similarity of these models to the colour model suggests a common source of origin. However, the model predicting the level of iron in runoff is remarkably similar to the colour model developed earlier. The same three variables are entered into both models, and in the same order. These independent variables also have gradients with the same direction and order of magnitude, while the

level of explained variance, with no standardised residuals dropped, is similar in both cases (colour 60.1%, iron 68.5%). The similarity of these models suggests that colour and iron do not merely share a common source of origin, but at least share a common process origin.

Further regression of colour, entering catchment morphometric and soils data, and all water quality variables produces the model:-

$$Log(Colour)=1.353(Fe)+2.07(\%TCLA_{05})+1.517(RV)+3.107$$

The level of explained variance in colour (r^2) entering iron only is 0.79, ($P < 0.00001$) with no residuals omitted. Entering the additional variables results in only a marginal improvement in the goodness of fit ($r^2=0.83$). This is strong evidence for a shared process origin between colour and iron. Furthermore the very strong positive relationship suggests that the complexation of iron in the colour structure is essential to the colour producing properties of the structure.

The complexation of iron by dissolved organic matter (DOM), has been reviewed by Mill (1980). There are strong parallels between the DOM-Fe and colour-Fe relationships and further serve to indicate that colour is largely composed of dissolved organic matter.

3.3.2.5 Conclusion

The seasonal pattern of colour in the Upper Burn valley is typical of upland catchments. Peak colour responds to

periods of high rainfall, and relatively dry antecedent conditions, suggesting that a colour flushing mechanism is operating in this catchwater. Significantly, there are differences in the spatial distribution of colour, with some catchments consistently contributing high colour levels to the reservoirs. This supports the conclusions drawn from the upper Nidd study (McDonald et al., 1990) and justifies a wider geographical application of colour reducing water resource strategies.

High colours were found to originate from the Winter Hill soil association, deep peat, which represents the greatest volume of organic matter in the catchwater. Some products of organic matter decomposition are soluble in water and it is thought these contribute to discolouration. Colour is also related to plateau areas (slope $\leq 5°$). In these areas hydraulic conductivities are generally low due to minimum gravity drainage, allowing maximum solute pick-up. When such areas have an intense drainage network the zone of aerobic decomposition is greater, producing a larger store of water colouring decomposition products. During periods of rainfall the intense drainage network allows a rapid movement of water, faster export of organic solutes and a more intense colour flush.

Particularly high colour was found to originate from areas of moorland burning and artificial ditching. This is consistent with observations on water colour in the Upper Nidd (McDonald et al., op. cit.) where it is suggested that

both these practices increase the zone of aerobic decomposition, producing a larger colour store. South facing slopes, associated with discoloration in the Upper Nidd were not found to be important in the Upper Burn. This is probably due to the largely North to North-Easterly aspect of the peat catchments.

A regression model can account for 60.1 per cent of the spatial variance in colour. This model uses variables that describe the extent of peat in the catchment, its gradient and the degree to which plateau areas are dissected. If catchments with evidence of moorland burning or ditching, influences not previously included in the analysis, the model can account for 81.6% of the colour variance.

Iron was highly correlated with colour. Regression analysis produces a model to predict aqueous iron of great similarity to that produced for colour. This indicates that colour and iron have a common source of origin in upland catchments, and suggests that iron may complexed with 'colour'. This complexation of iron may be essential to the fluorescent properties of upland water. The similarities in DOM-Fe and colour-Fe relationships suggests that colour is largely composed of dissolved organic matter.

3.4 Predicting the spatial distribution of coloured water.

A regression model, built from data collected for the upper Burn valley, uses catchment characteristics to account for variations in water colour. This model, M_u, has the form:-

$$Log_{10}Colour = 0.00512(\%TCLA_{5^\circ}) - 0.609(MSS) + 0.00368(\%1011b) + 0.21435 \quad (1)$$

Where for each sub-catchment the significant characteristics are:

$\%TCLA_{5^\circ}$ Per cent of Total Channel Length in area with slope ≤5°.

MSS Main stream slope[5]. Slope between 10 and 85 percentiles of main stream length.

%1011b Per cent catchment coverage by the Winter Hill Soil association

The performance of this predictive model was tested using data collected from the Upper Nidd valley. An accurate picture of the spatial distribution of colour in the How Stean catchwater of the Upper Nidd was determined from 32 separate snapshot exercises conducted between February 1986 and March 1987. This catchwater has a total area of 17 km^2. The mean observed colour at each intake along the catchwater, and the colour predicted by the model M_u are presented in table 3.12.

The difference between observed and predicted colour was analysed using a t-test (table 3.13) and a Wilcoxon matched pairs signed rank test (table 3.14). The t-test compares population means and is a measure of the degree to which the mean colour of the entire catchwater is predicted. The Wilcoxon rank test takes into account the relative magnitude of the individual cases that make up the catchwater mean and so measures the degree to which the

spatial distribution of observed and predicted colours match.

Table 3.12. Observed and predicted colour (aum^{-1} @ 400nm) at How Stean intakes, Upper Nidd valley.

Intake	Observed		M_u	M_d	M_{d+b}
	Mean	σ			
Armathwaite	10.37	(4.39)	5.37	4.59	21.00
Butts	2.67	(1.84)	1.40	1.20	1.43
Blackwell	4.92	(2.14)	1.42	2.15	4.64
Buskap	5.72	(5.52)	2.94	2.51	6.30
Crake	3.77	(3.30)	4.51	3.85	3.85
Aygill	6.46	(2.97)	4.58	4.34	4.34
Dunlin	6.99	(6.98)	1.59	3.61	3.61
Egret	7.64	(6.15)	2.80	8.64	8.64
Fieldeare	6.79	(3.18)	3.11	6.86	6.86
Staining	7.15	(3.14)	4.54	8.04	8.04
Blowing	4.45	(2.02)	3.54	5.89	5.89
Straightstean	3.72	(1.87)	4.61	4.97	4.97
Grouse	11.59	(5.69)	9.44	11.58	11.58
Backstean	4.75	(2.78)	4.65	4.69	4.69
Little Backstean	4.17	(2.47)	3.38	4.16	4.16
	N=32				

Table 3.13. Comparison of observed with predicted colour (au m^{-1}) levels along the How Stean catchwater.

		Association with obs colour			
	Mean	δ	R	t	2-tail prob
obs colour	6.0773	2.477	-	-	-
M_u	3.8587	2.001	0.6146	4.27	0.001
M_d	5.1387	2.715	0.6765	1.73	0.105
M_{d+b}	6.6667	4.655	**0.8000**	-0.75	0.468
	N=15	P < 0.01	P < **0.001**		

Table 3.14. Wilcoxon matched pair signed rank test of observed and predicted colour for How Stean.

Model	Z	2-tailed prob
M_u	-3.0670	0.0022
M_d	-1.1927	0.2330
M_{d+b}	-0.6248	0.5321

Both tests show that there is a significant difference between the observed and predicted colours using model M_u, although they are significantly correlated ($r=0.61$, $P<0.01$, $N=15$). The performance of model M_u is relatively poor, tending to under-estimate colour levels. This is attributed to the particularly high incidence of artificial ditching and moorland burning, previously identified as colour producing operations, practised on the How Stean catchments. The influence of these practices was not included in the original model construction. However, the

colour of water from four sub-catchments with low artificial drainage intensities and no evidence of moorland burning was predicted to within 1 au m^{-1}. This, and the significant correlation of observed and predicted values, indicates that the model M_u is likely to perform well in less intensively managed moorland catchwaters. This suggests that the significant factors determining the spatial distribution of colour have been identified.

However, intensively managed moorland catchments are likely to contribute the highest colour waters to reservoirs, and so from a catchwater management position, these colour yields should be accurately identified by the model.

Several sub-catchments in the How Stean catchwater have significant areas of ditching and it is these catchments that have marked deviation in colour yield from that predicted. Thus, the initial model, M_u, was weighted to represent the influence of moorland drainage. A spreadsheet was used to optimise model performance with the addition of a factor to represent drainage intensity. This was calculated as

$$f_{Di} = 0.1\ (\log_{10} Di + 0.854)$$

Where Di = Artificial drainage intensity in km/km^2

which when incorporated into the regression model produces a new model, M_d, with the equation:-

$$\log_{10} \text{colour} = 0.00512(\%TCLA_{5^\circ}) - 0.609(MSS) + 0.00368(\%1011b)$$

$$+ 0.1 \log_{10} Di + 0.29975 \qquad (2)$$

Such a development could not formally be incorporated into the multivariate framework because of its absence from the generative dataset.

Whereas definitive data on the areal extent of ditching could be determined at the application site, the influence of burning is much more difficult to quantify in terms of burn temperature, age and areal extent. The prediction power of the model can be significantly improved by the adoption of a multiplier (M_{d+b}) as below:

$$\text{Log}_{10}\text{Colour} = \{0.00512(\%TCLA_{5^\circ}) - 0.609(MSS) + 0.00368(\%1011b) + 0.1((\text{Log}_{10}DI) + 0.29975\} \times b \qquad (3)$$

Where b = 1 if no burning evident, 2 if burning is evident.

Because of the crude nature of the burning data available for testing the optimised model, the weighting is retained as a simple multiplier. Note, however, that 'burning' a sub-catchment does not result in the doubling of predicted colour, but acting through the log transformation yields an r value of 0.8 with observed colour.

The colour of water predicted by these weighted models for each intake is shown in table 3.12. Table 3.13 shows that both weighted models are able to predict the mean catchwater colour. Table 3.14 shows that both weighted models are also able to predict the spatial distribution of colour within the catchwater. This demonstrates that the

weighted models are successful in predicting water colour at each intake.

Model M_{d+b} produces the best prediction. The greatest errors are for Armathwaite and Dunlin intakes. Armathwaite intake is over estimated as the burning weighting is crude, simply presence or absence. Whereas the majority of the sub-catchments are small, Armathwaite is much larger. Thus, the presence of burning will, for most catchments, be a catchment wide influence but in the case of Armathwaite is likely to influence only part of the calculation. Including detail on the areal extent of burning should improve this prediction. Dunlin intake is under-estimated, possibly due to the high variance in the observed data.

Conclusion

Testing of the unweighted model demonstrates moderate success in predicting the spatial distribution of water discoloration. This demonstrates that the significant factors affecting the colour distribution have been identified. However, deficiencies in the model testing indicate that additional factors may be influential in determining the colour distribution. Burning and artificial ditching practices were identified in the Upper Burn as significant to water colour but were not included in the original model. Weighting this model by these factors greatly improves the predictive ability of the model and serves to illustrate their impact on colour. However, these weighted models should be tested on an

additional catchwater before application as a water resource tool. The application of these models to catchwater management and colour Hazard mapping is discussed in Mitchell and McDonald (1991).

3.5 Sub-catchment studies

3.5.1 'Micro-snapshot' exercise

A snapshot exercise was conducted in the Upper Nidd valley one day during September 1988. Water samples were collected from all the minor feeder streams contributing to runoff from the Armathwaite Gill sub-catchment (SE 075 748), and a further sub-catchment on South side of Angram reservoir (SE 034 754). These 'micro-snapshots' were conducted to determine whether the spatial distribution of colour varies over very short distances, and if so, if high colour flows originate in particular distinct areas. The data is illustrated in figure 3.6 (a,b).

The Armathwaite Gill sub-catchment shows a steady increase in colour from the intake to the moor top. The highest colours are found in areas with little evidence of recent ditching or burning and where gradients are very gentle. Water from the south feeder to Angram reservoir is less coloured than that from Armathwaite Gill, presumably due to the shallow depth of the organic soils on this steeper catchment. However, here too localised areas of high colour are evident, notably in feeders draining the Riggs moor plateau on the opposite side to Armathwaite Gill, and in the large marshy areas bounding the lower section of the

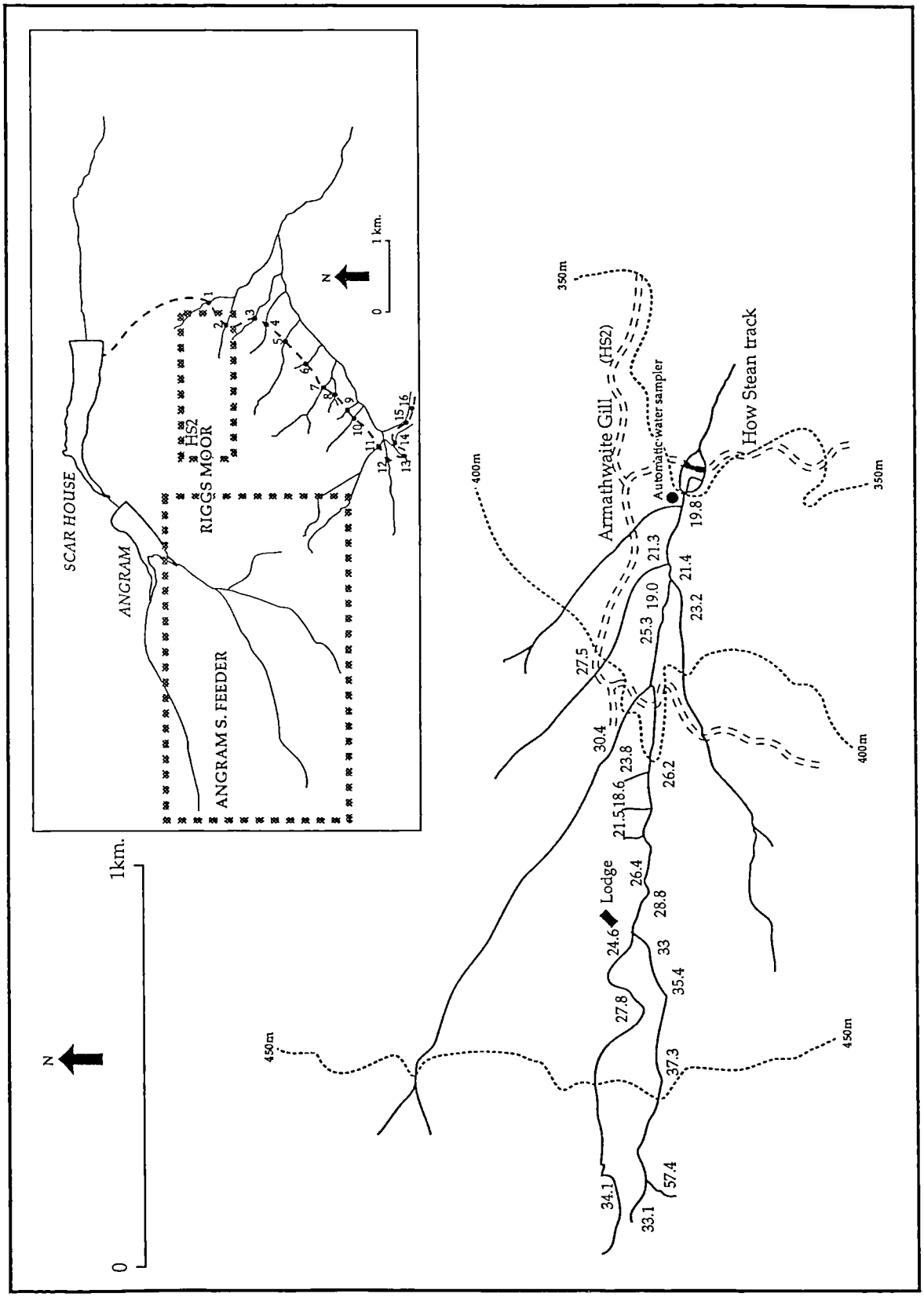


Figure 3.6 a Micro-snapshot: Spatial colour variation within Amathwaite Gill, Upper Nidd.

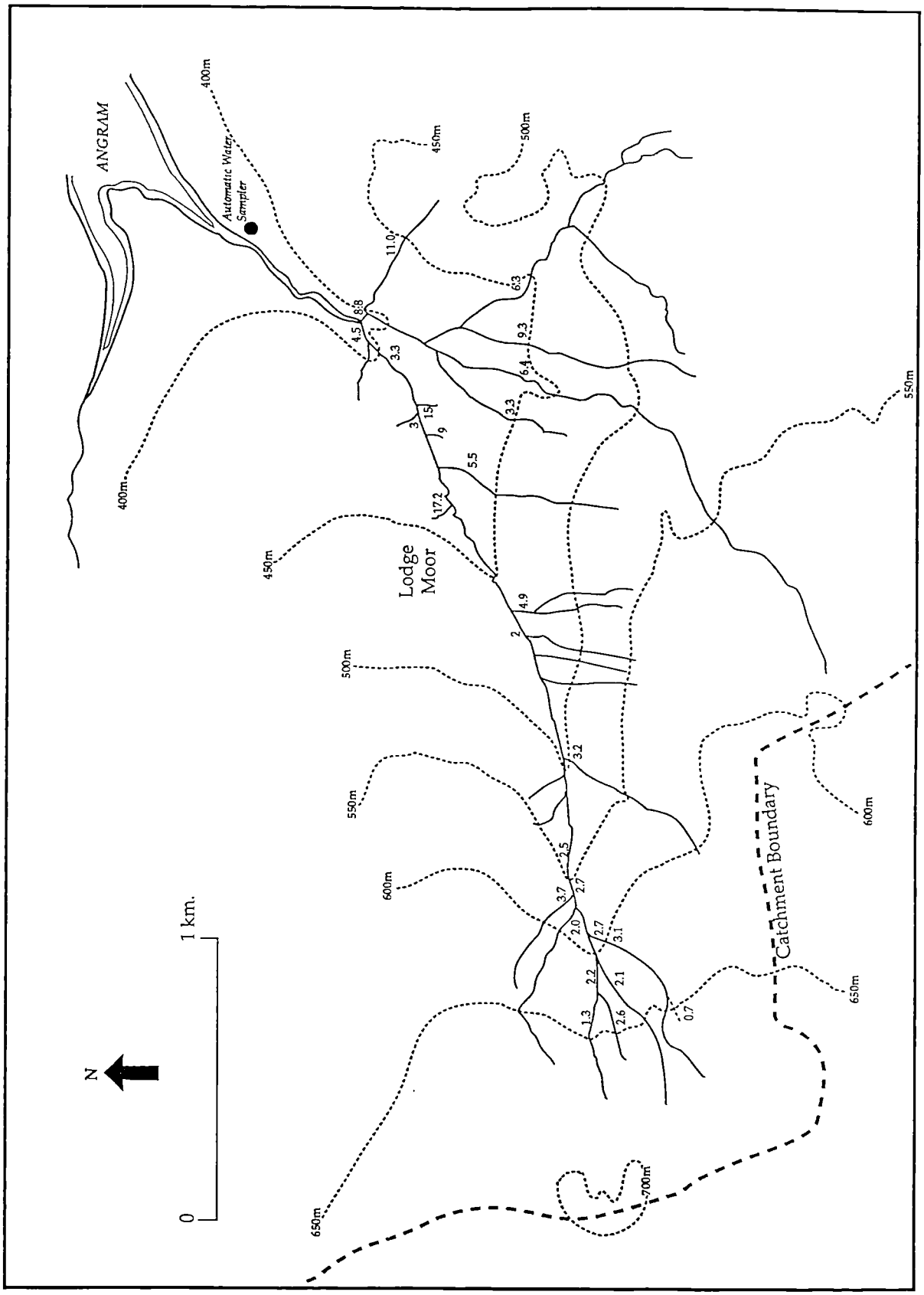


Figure 3.6 b Micro-snapshot: Spatial colour variation within Angram south feeder, Upper Nidd..

main feeder.

These observations demonstrate that even at this small scale, plateau areas constitute a major colour source area within peat catchments. They further suggest that the solubilisation of colour is enhanced by long water residence times in peat. Saturated peat areas, experiencing minimal gravity drainage, such as moor plateau and marsh produce a very large colour store which is released into supply very slowly, as hydraulic conductivities are very low. If drainage is increased, as a result of ditching for instance, then this colour store would be more rapidly depleted, producing very high runoff colours.

Although highest colours were found to originate from plateau areas, high colours were found flowing from burnt patches on the Armathwaite Gill catchment. These patches showed evidence of considerable heather regeneration and are likely to have been burnt several years previously. Water from the most recently burnt patch was of relatively low colour, and suggests that colour generation and release from areas of moorland burning is a prolonged process. This data is interpreted in the light of peat rewetting, and is discussed further in chapter five.

3.5.2 Colour investigations on severely eroded moorland

In the Derwent valley, Derbyshire, highly coloured waters were found to originate in areas of extensively eroded peat

moorland (McDonald and Naden, 1988). Boon et al., (1988) also identified eroded areas as a source of colour in the Elan valley catchments, Wales. Limited monitoring of water colour at Holme moss, West Yorkshire (SK 09 05) was conducted. This moorland suffers from severe erosion in places and has been designated as an environmentally sensitive area (ESA) in an attempt to promote revegetation and reduce erosion. This area was not suitable for grab sampling as there are few obvious streams draining the area. Therefore pieziometric wells were installed to monitor and so compare near surface ground water colour in eroded and vegetated (non-eroded) sites. Results are presented in table 3.15.

Table 3.15 Comparison of near surface ground water colour and depth in eroded and un-eroded peat moorland.

	Mean colour (au m^{-1})	σ	SE
Vegetated site	31.07	30.89	5.55
Eroded site	29.69	45.30	12.56
	t=0.12, df=42, 2t-prob=0.907		
	Mean depth (cm)	σ	SE
Vegetated site	71.80	32.19	5.78
Eroded site	56.92	40.37	11.20
	t=1.30, df=42, 2t-prob=0.202		

Results show no significant difference between water colour beneath eroded and vegetated sites. This may be attributed to water table depth, which does not vary

between site type, or it may reflect the limited data set. These eroded sites are relatively small and may not be of sufficient size to prevent compensatory water flowing from adjacent sites.

Consistent differences in colour were found between pieziometric wells, which is consistent with previous observations on the spatial distribution of colour. In addition the correlation between well depth and groundwater colour is significant ($r=0.7492$, $N=42$, $P< 0.001$). Wells with a lower water table may have higher water colour due to the great volume of overlying peat undergoing aerobic decomposition.

Erosion did not contribute to water discoloration at Holme moss. However, the analysis is based solely on data collected during the dry summer months. Any differences in water table depth and groundwater colour may not be detected until the water table rises and mobilises colour. Differences in colour may result from a differential rate in water table rise between eroded and vegetated sites. Eroded sites may take longer to reach field capacity due to lower rewetting potentials (chapter five), especially in the drier surface peat. Once surface peats do rewet, they may produce significantly more colour than the vegetated peats.

3.5.3 Additional sub-catchment studies

The North of England Grouse research project, part of the Game Conservancy, aims to assess the impact of

different land management practices on the regeneration of heather moorland. Much of this work is carried out at their Hall out moor site, Swaledale, North Yorkshire, where closely controlled drainage and revegetation strategies were implemented in 1986.

With the co-operation of the Game conservancy, ground water samples were collected from transects across recent ditch systems, and areas of burnt and unburnt moorland. Results indicate that, here too, consistent differences in colour are found between groundwater wells. Highest colours were found in areas of burnt moorland, where it is believed that sub-surface drying is enhanced, and close to grips where the water table is drawn down, and experienced greatest fluctuation. As at Holme moss, ground water colour was found to be inversely related to water table depth. A full account of the investigations at Holme moss and Gunnerside can be found in McDonald et al., (1990).

3.6 The spatial distribution of coloured water : Conclusion

The spatial discoloration of water was investigated at a variety of scales. A review of the available literature indicates that globally, the distribution of discoloured water is largely, but not exclusively, confined to temperate and cool temperate regions. These regions have mean monthly temperatures of 0°C to 30°C during the summer, and -30°C to 5°C during winter. Rainfall is in the range 600mm to 4000mm.

Within the UK discoloration was investigated on a regional

scale (c.7000 km^2), at the catchwater scale (c.60km^2), and at the sub-catchment scale (<1 km^2). At the regional scale the distribution of true colour is determined by the distribution of organic rich soil, specifically peat. The distribution of the Winter hill soil series, deep peat, accounts for the greatest proportion of the spatial variation in colour. The Belmont soil series, with a thin peat surface, is also significant. Thus the spatial distribution of water discoloration is largely determined by the volume of organic matter within a catchment. Rainfall is also important in determining the spatial distribution of colour, high rainfall is associated with high colour. These factors were able to account for 70% of the spatial variation in colour at the regional scale.

Some catchments are more susceptible to periods of high colour than others. This variation in water colour is also determined by the spatial distribution of peat, and rainfall. In addition, drainage intensity has a significant effect. An intense drainage network may promote high colour flushes by lowering the water table, producing a greater zone of aerobic decomposition and so a larger colour source area. A high drainage intensity may also permit a more rapid movement of drainage water, and therefore faster export of organic solutes.

The relationship between the spatial distribution of discoloured water and catchment characteristics was determined for an upland catchwater system in the Upper

Burn valley, North Yorkshire. Primary non-point sources of colour are identified as areas of Winter Hill peat with slopes $\leq 5°$, particularly those with high drainage densities. Heather burning and moorland gripping are identified as land management practices likely to increase water discoloration. These findings are consistent with those derived from earlier studies in the Upper Nidd and Washburn valleys and the Elan valley, (Boon et al.,1988). A regression model, weighted by moorland burning and artificial ditching practices was able to accurately predict the intensity and spatial distribution of coloured water, but requires further verification

At the sub-catchment scale high colours were observed in plateau areas. Peat in these areas experiences minimal gravity drainage and allows prolonged peat-water contact periods. This prolonged solubilisation of organic matter produces a very large colour store which is slowly released as runoff. A high drainage intensity in these areas promotes the removal of the colour store in response to rainfall, producing very high runoff colours.

Water colour and dissolved iron are strongly associated, and share a common source of origin. The similar nature of the Fe-colour and Fe-DOM relationships suggest that colour is largely composed of dissolved organic matter. Evidence further suggests that iron is complexed with the colour structure and may enhance the colour producing properties of dissolved organic matter.

4. THE TEMPORAL DISTRIBUTION OF COLOUR

4.1 Aims and Introduction

In chapter three the spatial distribution of colour was investigated. The results of this chapter demonstrated that there are consistent differences in colour between catchments, and that the intensity of colour from these catchments can, to a certain degree, be predicted. These predictions are based on information that characterises the catchments; soil type, drainage intensity, slope and burning practices. Changes in these characteristics results in a change in the colour of water draining a catchment. For example, runoff colour increases following the execution of moorland ditching and burning practices. Peat accumulation, in terms of pedogenesis, may also increase colour. However, such colour changes are the result of either short or very long term modifications to catchment characteristics, and act to produce a new colour equilibrium. They cannot therefore account for the seasonal distribution of colour commonly observed for upland catchments. This is especially true in those catchments where intensive moorland management operations have not been practised.

All upland catchments experience some degree of fluctuation in runoff colour, which cannot be attributed to changes in catchment characteristics alone. All catchments respond in a broadly similar manner, with low colour during the summer and peak colour during the autumn. The commonly

observed and consistent annual pattern of water discoloration is a clear indication that climate is the single most significant factor determining the temporal distribution of water discoloration. In addition, previous analysis (section 3.2) showed that, at the regional scale, the spatial distribution of discoloration is significantly influenced by climate. In particular, the spatial distribution of rainfall has a clear impact on the spatial distribution of colour. It is assumed therefore, that climatic variables, such as rainfall, with high seasonal variations are likely to be influential in determining the seasonal variations in colour.

In this chapter, an attempt is made to define the temporal distribution of colour, and determine the nature and impact of the climatic factors thought to influence that distribution. The temporal distribution of colour is studied at a variety of scales. In the first section raw water colour at several south Pennines treatment works draining large basins is examined. In the second section a more detailed analysis is performed for a single catchwater system, while in the third section an analysis of individual storm events is presented. Finally, the temporal pattern of colour at the smallest scale, a peat throughflow pit is investigated. Evidence is presented for seasonality in the complexation of colour and iron.In addition, some further points, detailing the influence of catchment characteristics on the temporal distribution of colour are made.

4.2 Analysis of long term colour records

Due to reorganisation of water utilities, particularly in 1974 and 1989 there are few long term records of water colour. Most available colour records date from the mid to late 1970's, and many do not begin until the early 1980's. The colour record analysed in this section covers the period 1961-1979 and is the longest known colour record at present. Raw water colour was measured at treatment works receiving water from six reservoirs in the southern Pennines, supplying the Sheffield conurbation.

The pattern of colour for each site is illustrated in figure 4.1. It is apparent that there are some deficiencies in the data, particularly with the early part of the record. Up to circa 1968 colour values ≤5 and ≥70 Hazen are determined incorrectly due to the measurement technique adopted at that time. Given that the unit of colour in these records is Hazen it is probable that colour was also determined by an apparent colour method. Problems of colour measurement are discussed by Mitchell and McDonald (in press). Despite these difficulties observations can be made about the temporal distribution of colour from these records.

Descriptive statistics are presented in table 4.1. The high standard deviations (in relation to mean colour values) indicates that the temporal distribution of colour is highly variable. Skewness and kurtosis indicates that in most cases colour approximates to the normal distribution

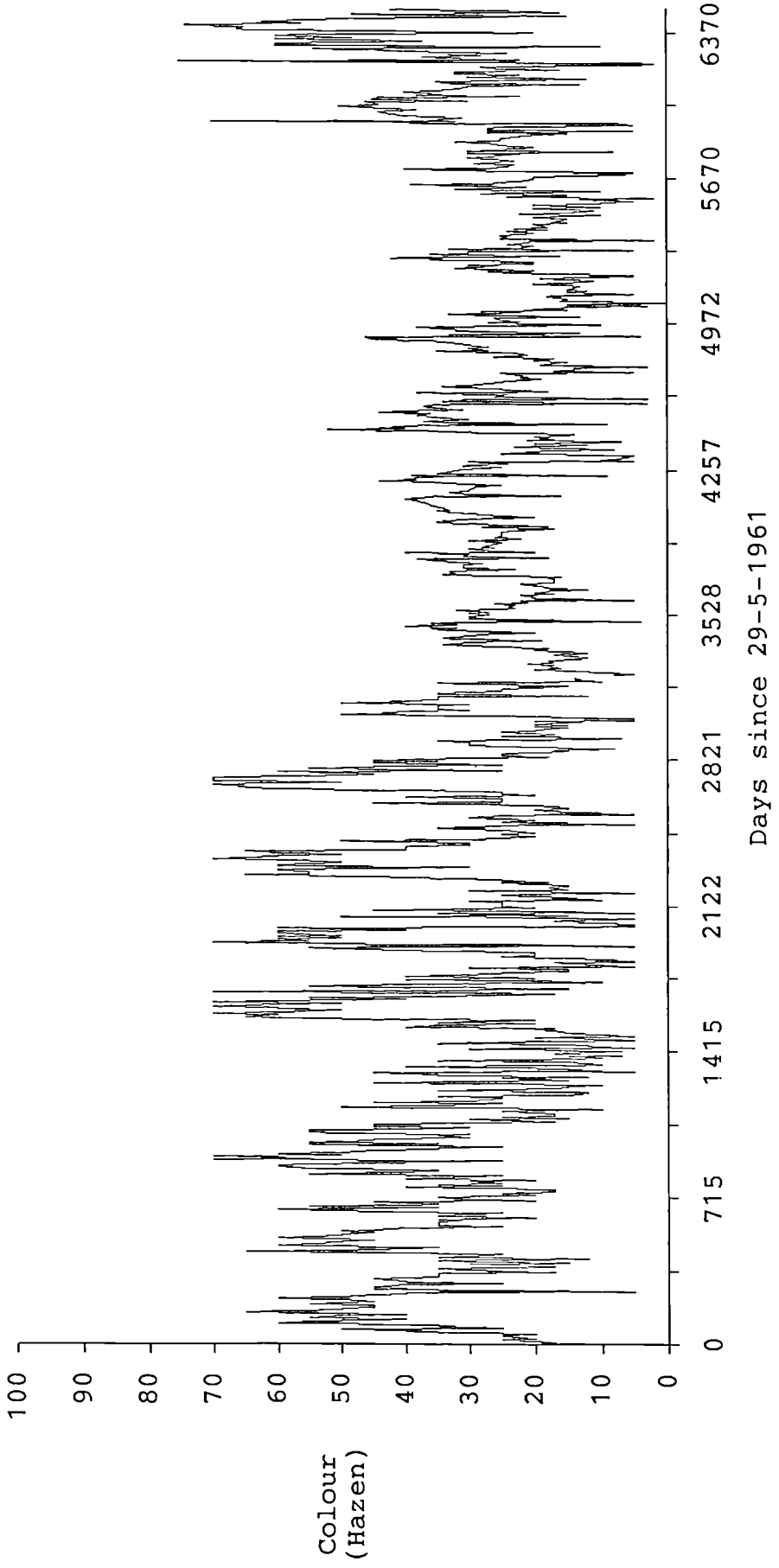


Figure 4.1 Raw water colour at Rivelin water treatment plant, 1961-1979

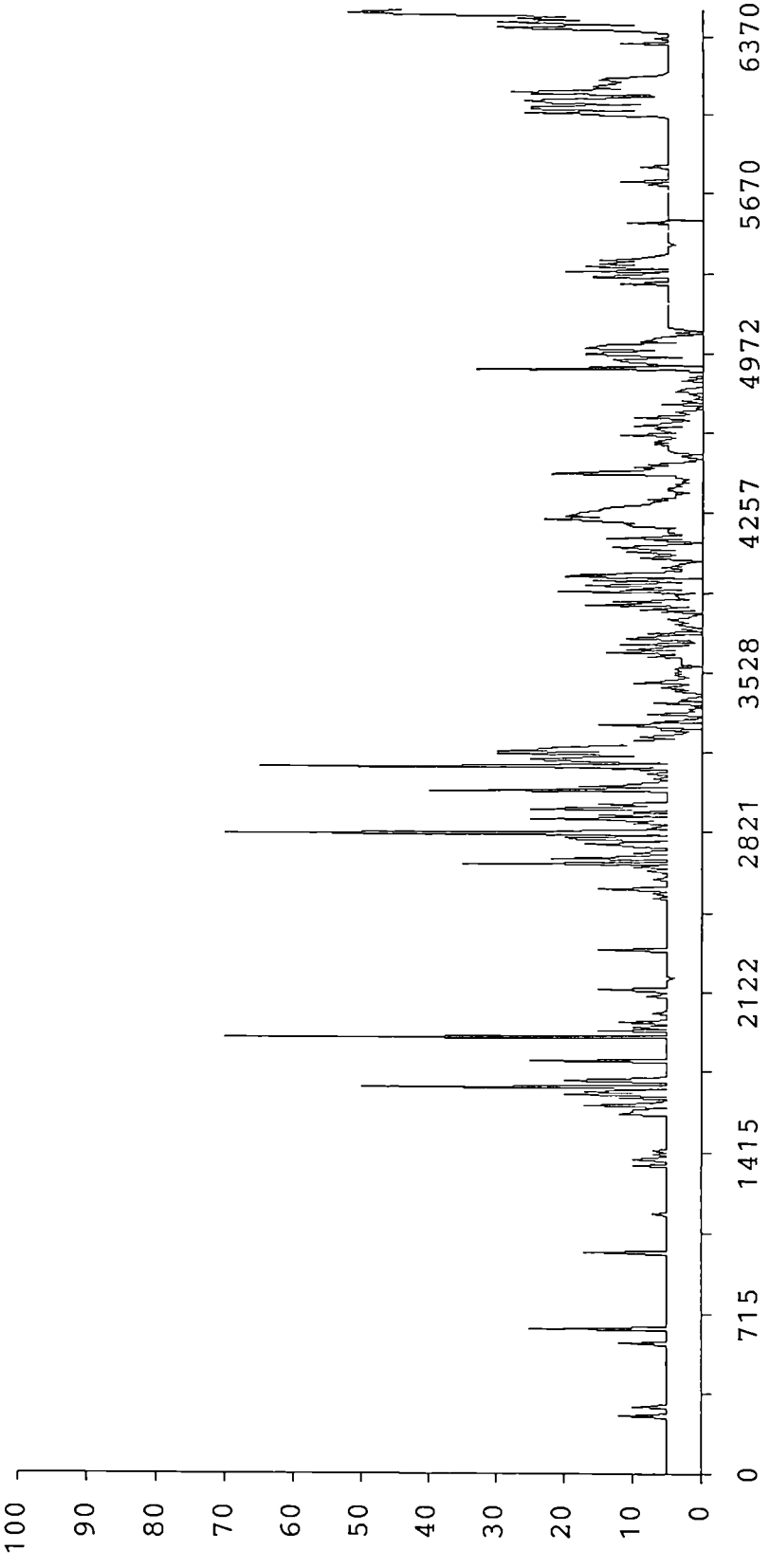


Figure 4.1(cont.) Raw water colour at Redmires water treatment plant, 1961-1979

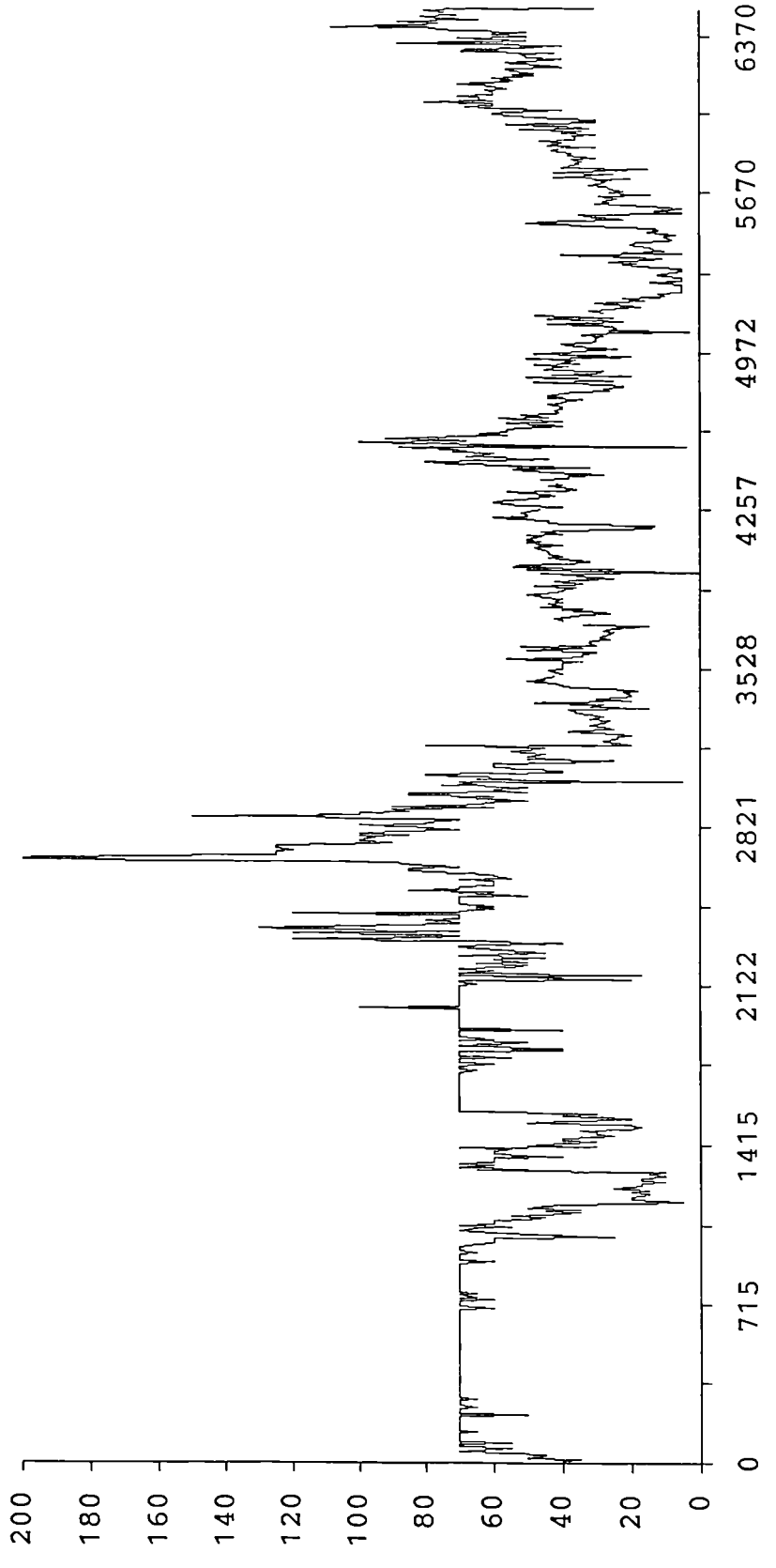


Figure 4.1(cont). Raw water colour at Langsett water treatment works ,1961-1979

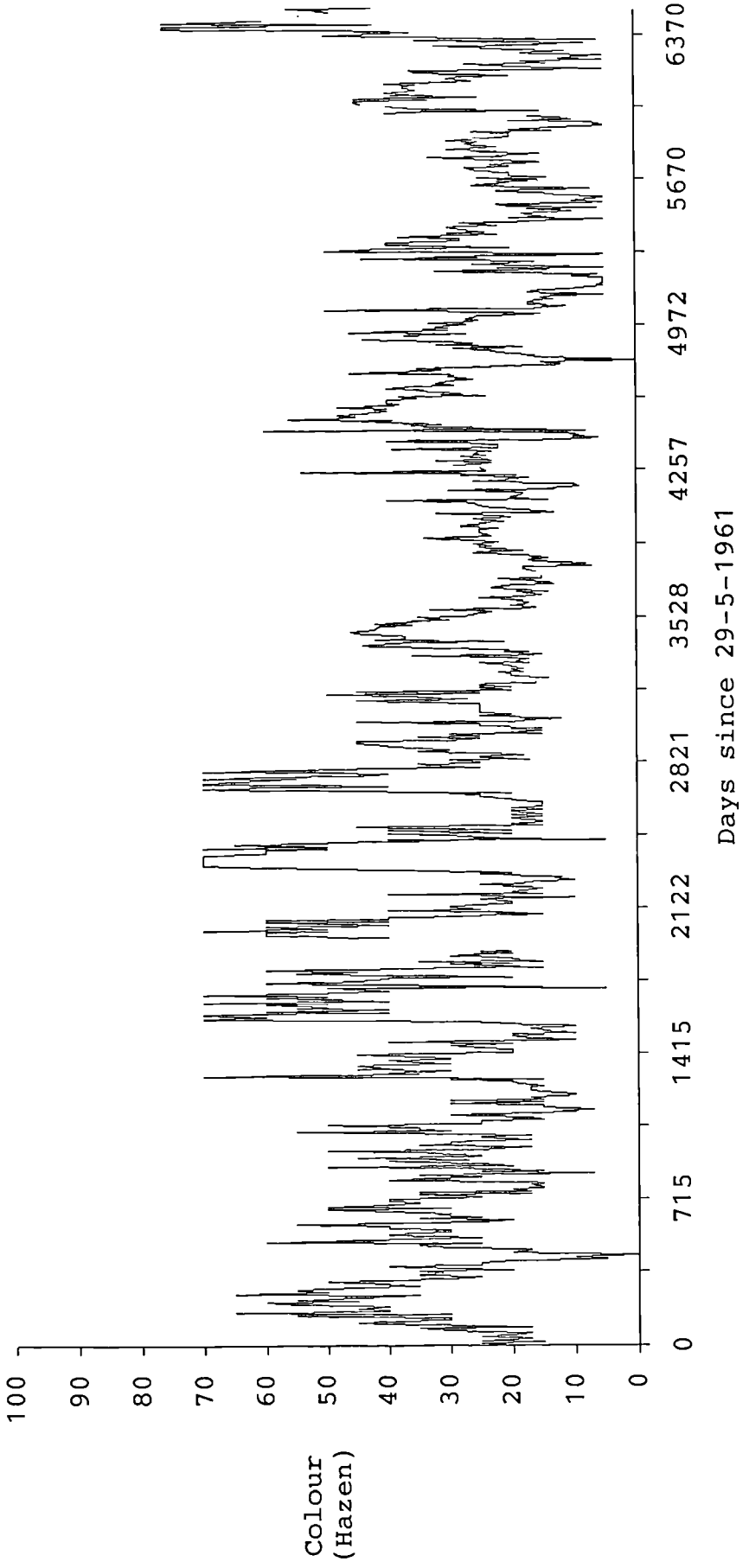


Figure 4.1 (cont.) Raw water colour at Agden water treatment plant 1961-1979

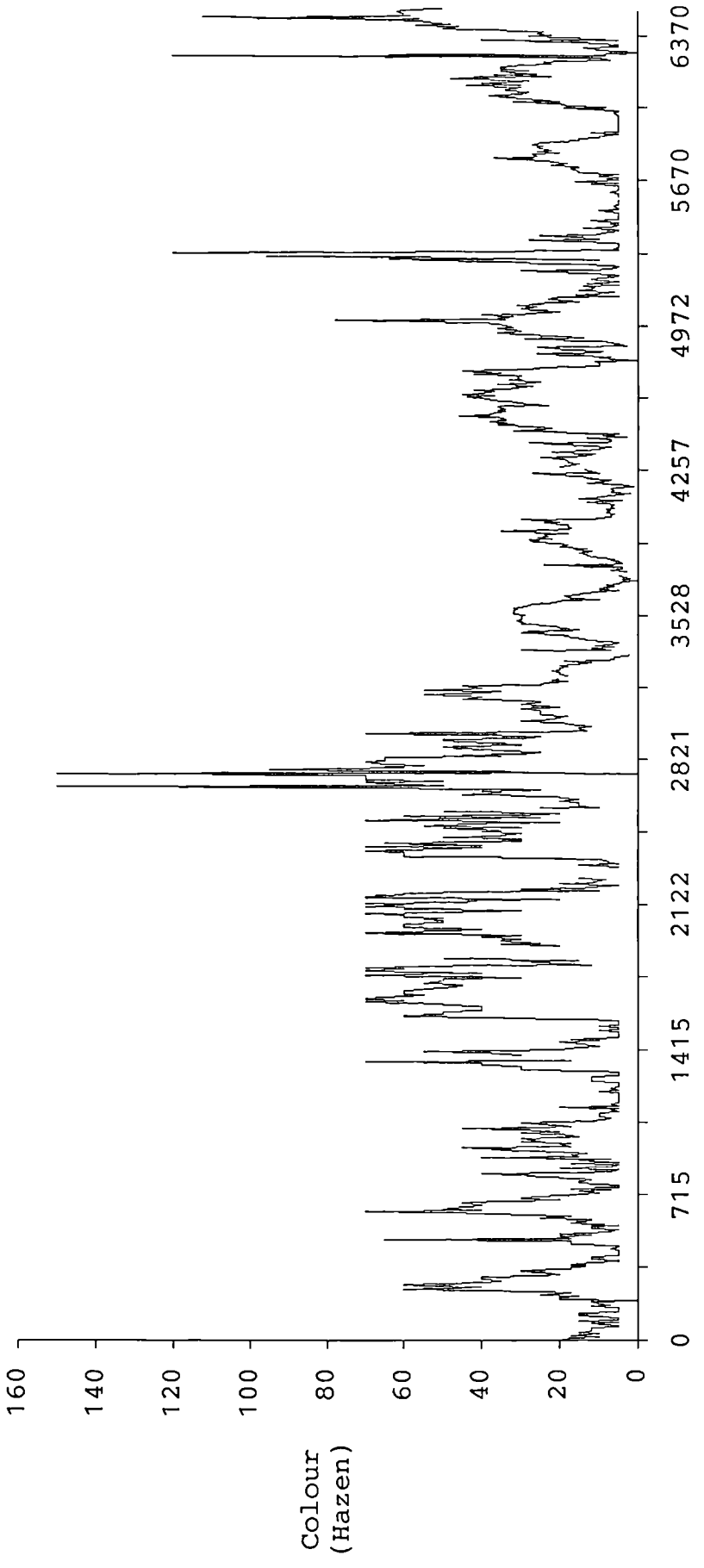


Figure 4.1(cont.) Raw water colour at Dale dike water treatment plant 1961-1979

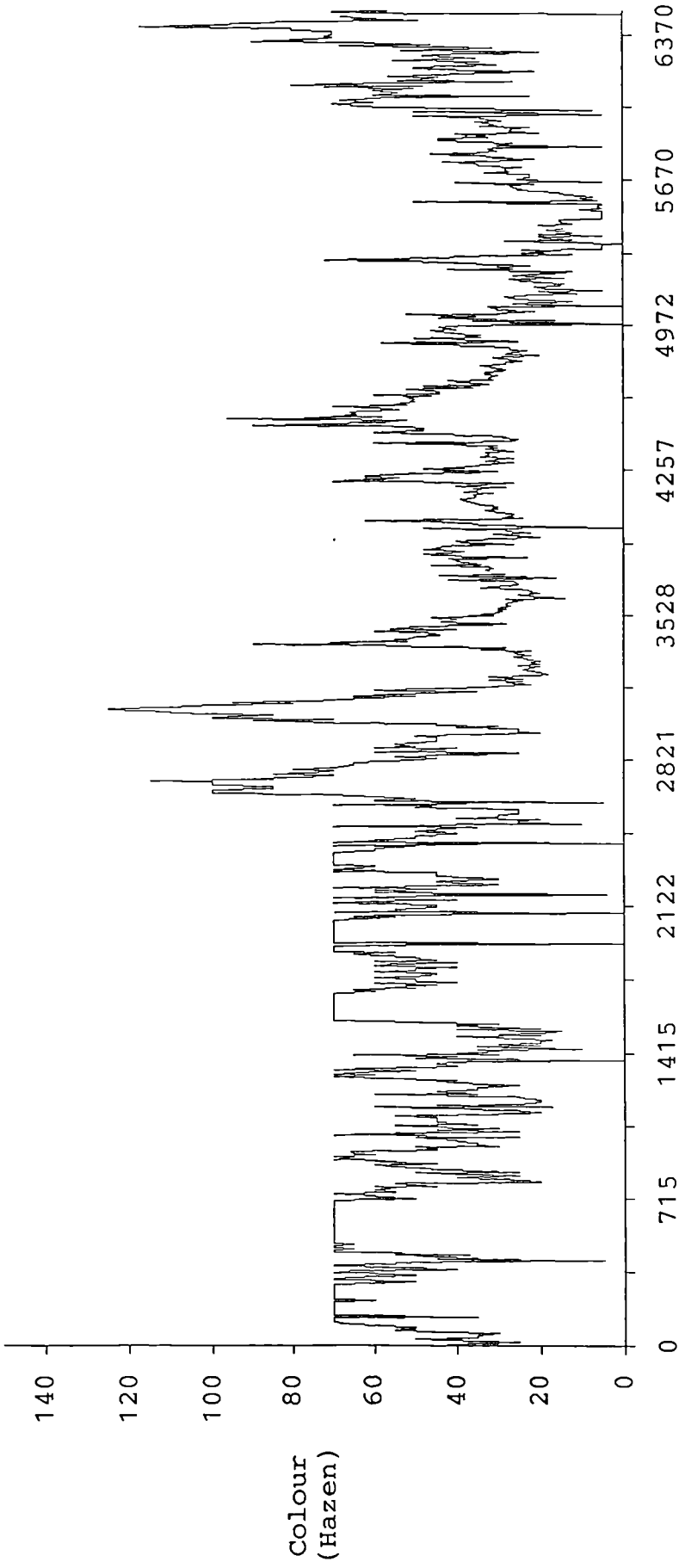


Figure 4.1(cont.) Raw water colour at Ewden water treatment plant 1961-1979

curve. The exceptions, particularly Redmires, are thought to be a product of deficiencies in the data, rather than any real deviation.

Table 4.1. Descriptive statistics for southern Pennine colour (Hazen) records, 1961-1979.

Reservoir	Mean	σ	Min	Max	Kurtosis	Skewness
Agden	28.9	14.8	0	76	0.45	0.85
Dale Dike	24.6	19.8	0	150	4.45	1.59
Ewden	45.0	21.6	0	125	0.04	0.39
Langsett	51.7	24.6	0	250	5.71	1.01
Redmires	7.2	7.0	0	70	24.85	4.13
Rivelin	29.7	15.3	0	75	-0.34	0.62

For each record there is a clear annual pattern. Lowest colour values occur during summer and highest colour values during the autumn-winter. This seasonal pattern is more clearly seen in figure 4.2 which shows weekly average colours over the period of record. To demonstrate that the annual colour cycle is approximately sinusoidal each colour record was correlated with the output of a simple harmonic function. This function took the form:

$$S_a = 1 + \{\cos (2\pi (D_1 + D_2/365))\}$$

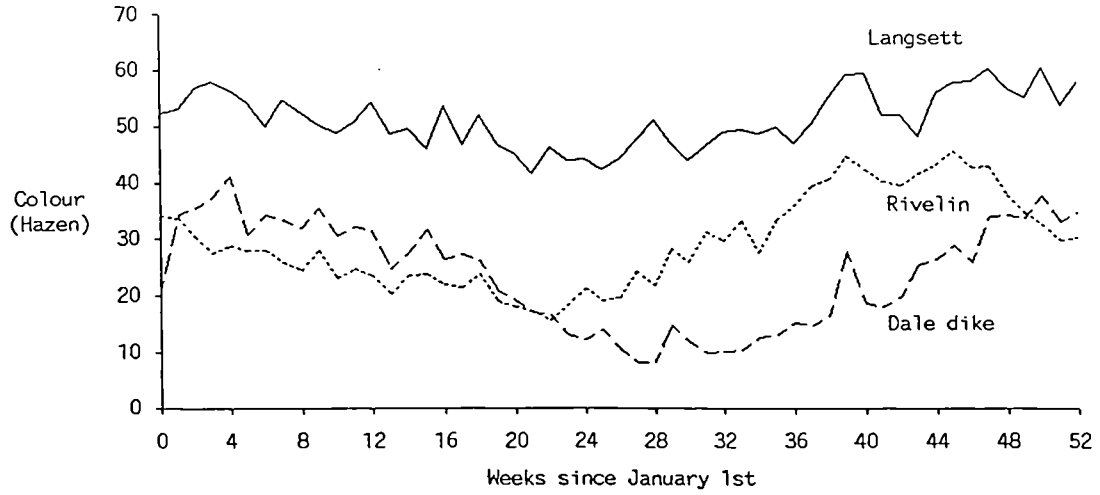
S_a = Sine wave with wavelength of one year.

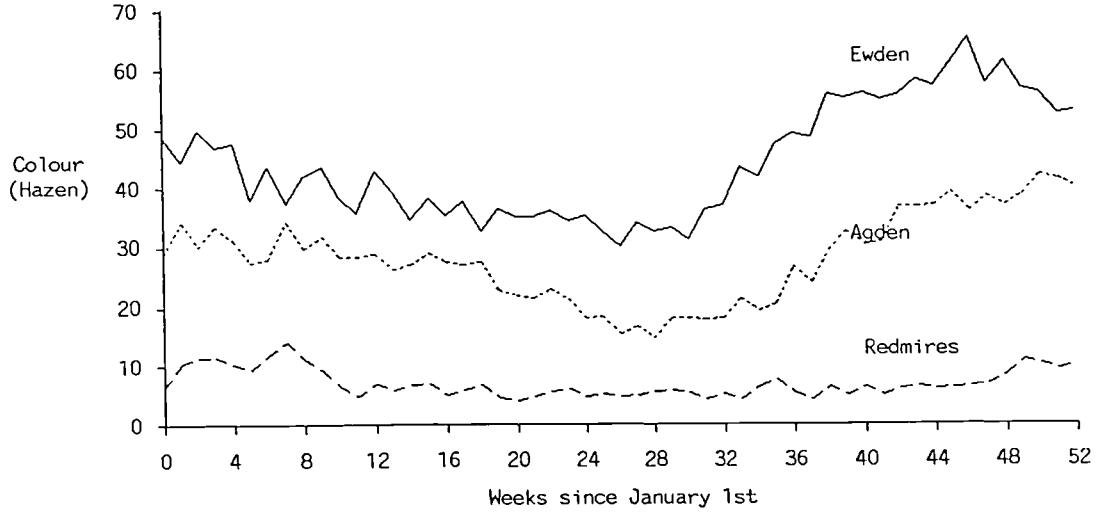
D_1 = the number of days since Jan 1st 1961.

D_2 = number of days until Dec 31st.

By altering D_2 the phase of the resultant sine wave can be

Figure 4.2 Mean weekly water colour for selected south Pennine WTWs, 1961-1979.





controlled. The peak of the generated wave is always at D_2. Many such waves were generated in an iterative procedure and correlated with each of the six colour records for the full 18 year period. The results are presented in table 4.2.

Table 4.2 Pearson correlation (r) of generated sine wave (S_a) with southPennine colour records, 1961-79.

	Maximum Correlation coefficient (r)	D_2	Approximate time of year
Agden	0.4412	365	Early January
Dale dike	0.4551	335	Late January
Ewden	0.4067	35	Late December
Langsett	0.1653	5	Late December
Redmires	0.2801	335	Late January
Rivelin	0.4851	55	Early November

$P < 0.001$, N=919

This analysis demonstrates that each record exhibits a clear sinusoidal colour pattern with a frequency of one year. The maximum correlation coefficient ($P<0.001$) is found at the point where the colour record and generated wave are in phase. This point is always between November and January, indicating peak water colour is consistently observed during this period. This pattern suggests that water discoloration is a process determined by seasonal climatic variation. Precipitation and temperature may significantly affect runoff colour through catchment

flushing during the relatively cold and wet autumn-winter, while the colour store is replenished during the relatively warm and dry summer period.

Table 4.3 Variation in southern Pennine annual average colour (Hazen), 1961-1979.

Year	Langsett	Rivelin	Redmires	Ewden	Agden	Dale dike	N
1961	62.5	40.1	5.0	55.5	31.3	10.6	30
1962	69.4	39.2	5.3	62.3	34.0	20.6	51
1963	69.2	38.5	5.5	57.5	30.8	22.7	52
1964	40.8	30.6	5.3	40.1	44.3	13.1	53
1965	40.8	30.0	6.6	45.3	35.4	29.8	51
1966	67.5	31.4	9.1	59.5	41.6	47.2	52
1967	68.2	34.8	5.5	54.7	36.4	39.2	52
1968	88.0	34.2	7.2	56.9	34.2	45.8	53
1969	69.9	27.2	12.1	63.3	28.0	35.6	51
1970	33.8	22.5	7.3	36.4	28.8	20.6	51
1971	36.2	24.5	4.5	31.9	19.4	14.5	49
1972	40.4	29.8	7.1	35.5	22.4	13.7	50
1973	54.3	25.1	7.3	45.8	31.3	23.0	50
1974	40.0	24.6	4.2	35.8	27.8	24.9	51
1975	21.7	19.7	6.8	25.5	18.4	26.0	51
1976	19.1	18.4	6.3	14.2	20.1	7.4	52
1977	38.8	29.6	6.9	34.3	23.5	15.2	52
1978	59.1	37.51	11.0	54.1	29.8	29.3	52
1979	70.6	39.4	31.4	66.0	55.9	63.0	10
LTA	52.6	30.4	8.1	46.0	30.2	26.4	

Although the seasonal pattern of water discoloration is highly consistent, the year to year variation is not. Table 4.3 shows the annual average colour at each water treatment works. For some years the annual average colour is less than half, and for some years more than double the long term average (LTA) over the full period of record. This represents a massive fluctuation in the degree of water discoloration experienced at these sites. Assuming that annual water demand is constant, considerable variations in annual colour fluxes are evident.

Table 4.4. Trends in south Pennine water colour, 1961-79.

	Correlation with DAY	Regression with DAY	r^2 (%)	Prob F<
Agden	-0.1880	Colour= -1.5DAY+33.8	3.7	0.0001
Dale dike	-0.0588	Colour= -6.5DAY+26.9	0.4	-
Ewden	-0.3375	Colour= -3.9DAY+57.6	11.5	0.0001
Langsett	-0.3890	Colour= -5.1DAY+68.2	15.1	0.0001
Redmires	0.1543	Colour= 5.5DAY+ 5.4	2.1	0.0001
Rivelin	-0.1923	Colour= -1.6DAY+35.1	4.0	0.0001

DAY = Number of days since 29th May 1961

There is a clear increase in annual average colour at each site from 1976 to 1979. Such increases in colour fuelled concern amongst water managers that colour was exhibiting a rising trend. However, on the basis of this data it is apparent that throughout the 1970's colour was very much lower than throughout the 1960's. The increase in colour at the end of the 1970's is actually part of a general downward trend in colour during 1961-79 (table 4.4). Five

of the six records studied exhibit a significant ($P<0.0001$) downward trend. However, this downward trend may just be part of a larger colour trend exhibiting periodicity over many years. The rapid increase in colour towards the end of the 1970's is widely believed to be a consequence of the prolonged drought of 1976.

The annual distribution of colour is determined by the seasons which are determined by the position of the sun. Maximum annual colour in the UK is always found near aphelion, when the sun is farthest from the northern hemisphere. In a similar way the long term trends in water colour may also be determined by other longer term astronomical cycles, such as the 11.77 year sunspot cycle. However, it is not possible to determine the existence of any cycles longer than a year given the lack of available long term records.

4.3 Analysis of scar outflow record

In this section an analysis of water colour at the outfall from the How Stean-In moor catchwater to Scar House reservoir (Upper Nidd) is presented. The outfall (SE 065 767) drains approximately 30 Km^2 of moorland.

There are several advantages of this analysis over the analysis of the long term records above. Firstly true colour is measured, and at a high frequency. Throughout the study period, October 1985 to July 1989 samples were collected at 12 hourly intervals by automatic sampler.

Secondly, colour measurements are taken upstream of the reservoir and so exclude any lag times induced by reservoir processes. Thirdly, a permanently installed flow monitor was able to give a record of discharge simultaneous with colour. During the study period a mean daily discharge of 43.8 TCM (thousand cubic metres) was recorded. Records of daily rainfall at Scar House for the study period were available courtesy of Yorkshire Water. Mean annual rainfall for the area, during the study period, was 1410 mm.

The record of water colour at the How Stean-In Moor outfall is illustrated in figure 4.3. Colour is highly variable throughout the record but shows a clear seasonal distribution. Highest colours are observed during the autumn and lowest values during the summer months. A highly significant correlation exists between water colour and a generated sine wave ($r=0.3429$, $N=713$, $P<0.001$). This maximum positive correlation exists when the value of D_2 is 72, which places the colour peak in late October. This is slightly earlier than the colour peaks found in the southern Pennine data set and may be indicative of reservoir induced lag times in that data. Colour was found to reach a minimum in late April.

Descriptive statistics of colour are presented in table 4.5. These indicate that water colour rarely drops below the EC potable water standard, and that cumulatively there are several weeks a year when colour exceeds this standard by an order of magnitude.

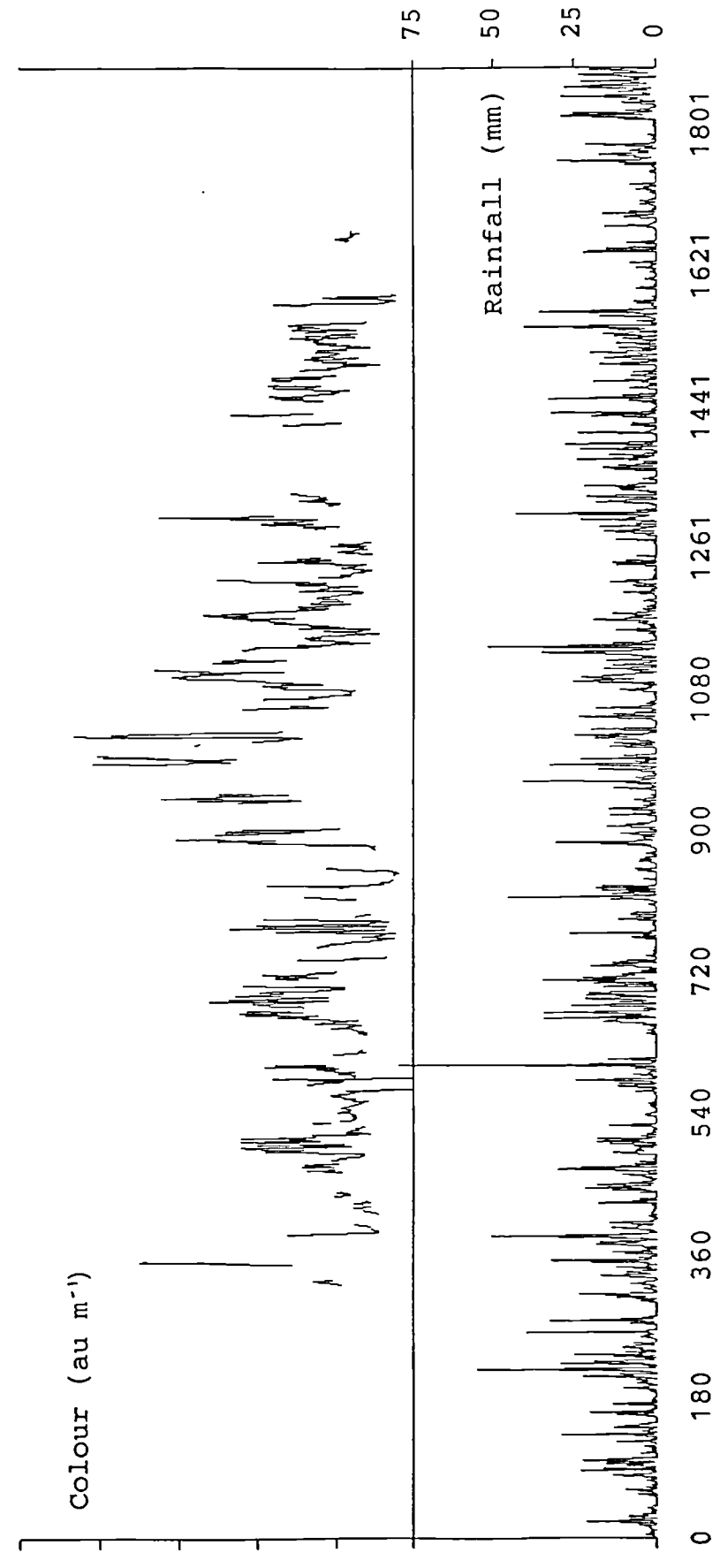


Figure 4.3 Daily colour and rainfall record for the How stean reservoir outfall, Upper Nidd, November 1985-July 1989

Table 4.5 Descriptive statistics for How Stean-In Moor outfall, October 1985 - July 1989.

(i)	Mean	σ	Min	Max	Kurt	Skew
Colour (au m^{-1})	6.40	3.44	1.0	21.7	2.23	1.33
Rainfall (mm d^{-1})	3.86	6.91	0.0	79.6	16.59	3.29
Discharge (TCM d^{-1})	43.79	81.76	0.0	1109.0	68.29	6.87

(ii)	Colour (au m^{-1})	Percentile	Days yr^{-1} colour value exceeded
EC standard	1.5	2.3	356
Mean colour	6.4	61.1	142
Mean + 1σ	9.8	85.6	53
Mean + 2σ	13.2	95.5	16
Mean + 3σ	16.6	98.2	7
Mean + 4σ	20.0	99.5	2

The seasonal distribution of colour at the outfall is typical of many other Yorkshire catchments, exhibiting a broadly predictable pattern, determined by local precipitation. However, the day to day variation in colour is highly variable, and much less consistent.

For the entire data set mean daily colour was found to be strongly correlated with daily discharge ($r=0.2685$, $N=737$, $P<0.001$) and precipitation rates ($r=0.2054$, $P<0.001$, $N=737$). However, maximum correlation coefficients occurred when the colour data was lagged with respect to discharge and precipitation. The lag times were two days for

precipitation ($r=0.3187$, $P<0.001$, $N=737$) and one day for discharge ($r=0.2338$, $P<0.001$, $N=737$). This suggests that antecedent rainfall and discharge are influential in determining water colour, and is consistent with colour removal by catchment flushing. The resolution of the data does not allow more accurate determination of colour response to discharge and ultimately rainfall.

If the colour data is split about the mean (6.4 au m^{-1}), no correlation is found between colour and precipitation or discharge on days of above average colour. However, below average colour is significantly correlated with both precipitation ($r=0.1487$, $N=450$, $P<0.001$) and discharge ($r=0.1863$, $N=417$, $P<0.001$). Periods of below average colour have significantly lower, less variable precipitation ($t=9.635$, $df=292$, $P<0.001$) and discharge ($t=7.413$, $df=279$, $P<0.001$) than the above average colour periods. The precipitation and discharge distributions are also highly kurtose and positively skewed (table 4.5). These observations suggest that during periods of low rainfall and discharge, colour has a low variability, achieving a degree of 'equilibrium' and so correlates well with rainfall and discharge. Conversely periodic storm events are associated with rapidly changing rainfall and discharge regimes. These are thought to be associated with high colour flows but are not well correlated with them due to the slow colour response time.

4.4 Response to short duration storm events

The variation in discharge colour for a small peat catchment was studied. The catchment, drained by Armathwaite Gill, Upper Nidd (SE 070 750) has an area of 194 ha and is part of the How Stean-In Moor catchwater feeding Scar House reservoir via the outfall studied in 4.2 above. Throughout the study period, November 1989 to February 1990 (100 days) water samples were taken at eight hour intervals. This represented the 'background' sampling rate. The automatic sampler was connected to a float switch which, triggered by a rise in stage height, increased the sampling frequency to one sample per hour. The sampling continued at this new frequency, irrespective of discharge, until all sample bottles were used or the sampler was serviced. The sampler was serviced on a weekly basis. This sampling regime allows colour to be monitored at a low intensity during periods of low flow when colour varies least, and at a greater intensity during periods of high flow.

Stage height was recorded continuously throughout the study period, but no rating curve was produced. This was due to the difficulties associated with accurately measuring discharge in small streams, including the possibility of bed scouring during periods of high flow. It would also have proved difficult to obtain sufficient discharge measurements at periods of high flow when operating an automated sampling regime with minimal servicing.

Similar event based studies, investigating the variation in dissolved organic matter (DOM) with discharge have been conducted (Fisher 1970; Foster and Grieve, 1982; Grieve, 1984). Although a high correlation between absorbance and DOM in a stream draining a peat catchment has been demonstrated (Grieve, 1985), there are several reasons why colour and DOM cannot be considered directly comparable for event based studies. Firstly, researchers measuring DOM by absorbance do so at 360 or in the range 200-254 nm '. These wavelengths are in the UV-spectrum, and so are not comparable to colour which is measured at 400 nm , firmly in the visible wave range. Secondly, unlike colour, DOM has a peak absorbance, at 254 nm . Finally, the temporal distribution of individual colour forming organics is unknown. It has been demonstrated for a humic lake in the Netherlands that the E_{250}/E_{365} absorbance ratio varies seasonally (De Haan and De Boer, 1987) suggesting that the concentration of different organic species also varies seasonally. The ability of these individual organic species to discolour water is unknown, but has been shown to vary with cation availability (Shapiro, 1964; Straumanis, 1962; Theis and Singer, 1973; Tipping, 1987). Measures of DOM cannot reflect the variation in the propensity of different organic species to discolour water.

The variation in daily rainfall, stage and water colour for Armathwaite Gill during the study period is shown in figure 4.4. Mid November to mid December 1989 was a dry period, with little runoff. Water colour during this period was

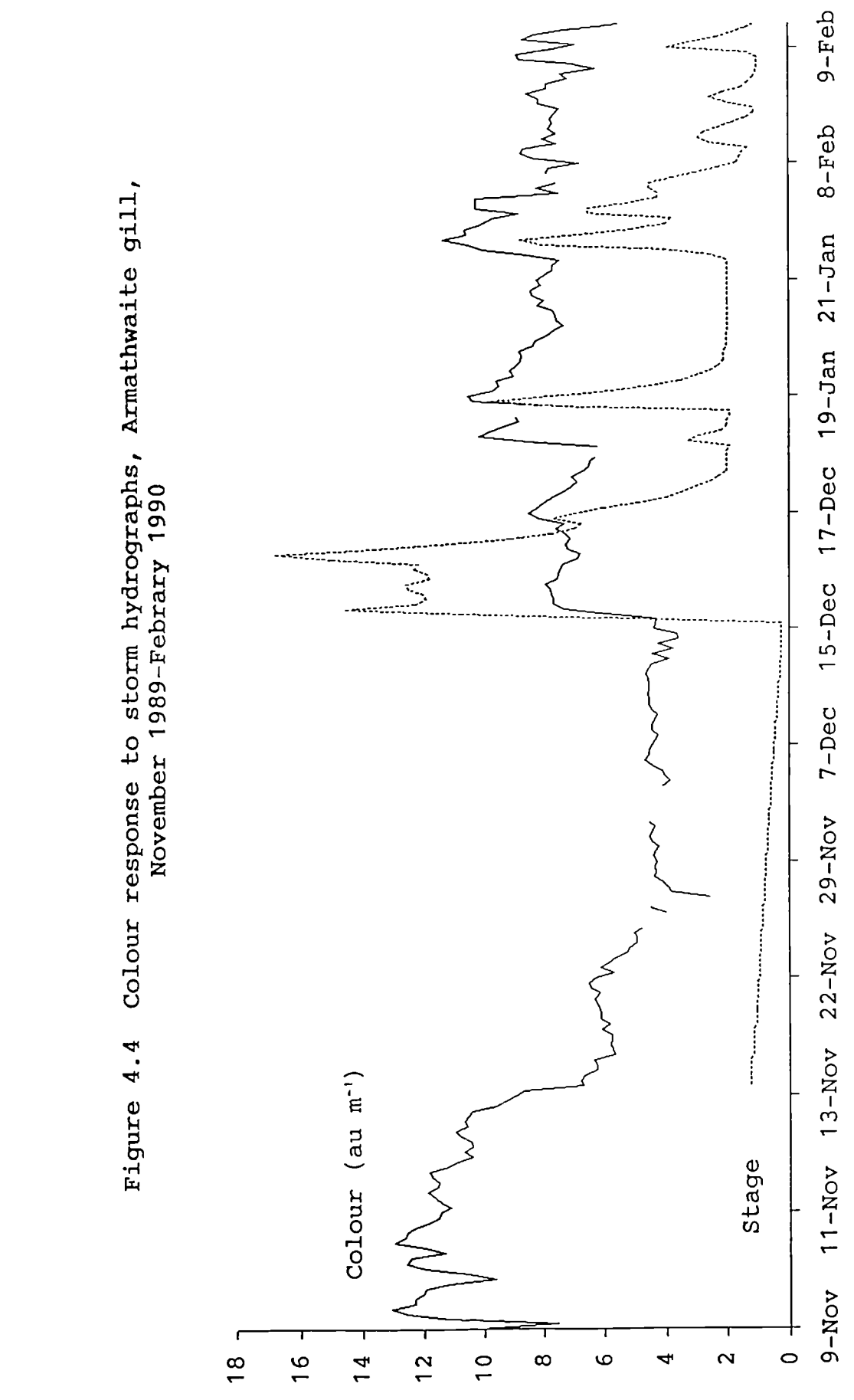


Figure 4.4 Colour response to storm hydrographs, Armathwaite gill, November 1989-Febrary 1990

relatively stable around 4 au m^{-1}. A series of storm events from mid December to the end of the study period are coincident with an approximate doubling in colour. This moisture regime is analogous to the longer seasonal cycle, where a large proportion of total annual water colour occurs in the wetter months following summer.

Table 4.6 Relative colour difference in Armathwaite Gill during periods of low and storm flow.

	Stage (units)	Mean colour (au m^{-1}) (a)	Mean stage (b)	Product (a x b)
Low flow	< 2	4.719	1.280	6.04
Storm flow	> 2	7.784	7.779	60.55

Table 4.6. demonstrates the difference in water colour between periods of low and high discharge. High discharge was defined, with reference to figure 4.4, as discharge above two stage units. Water is significantly more coloured during these high flow periods ($t=36.09$, $df=78$, $P<0.001$). The product of stage and colour indicates that the colour flux is an order of magnitude greater during periods of high flow. This suggests the operation of a mechanism 'flushing' organic solutes from the catchment.

A significant difference in water colour is also found between periods of rising and falling stage. Colour is greater on the falling hydrograph limb ($t=2.915$, $df=118$, $P<0.01$) indicating that colour lags behind discharge.

Colour has a strong positive correlation with both daily

rainfall and stage. However, the maximum correlations are found when rainfall and stage are lagged with respect to colour (table 4.7). During the periods of high discharge colour lagged one hour behind discharge and six hours behind rainfall. This analysis demonstrates the sequence and timing of the rainfall-discharge-colour responses operating in the catchment. It is inferred that during the study period discharge lagged five hours behind rainfall. However, it was not possible to accurately determine lag times with respect to rainfall, due to the resolution of the rainfall data. It is likely that the rainfall-discharge response time varies seasonally, dependent upon soil moisture status. This implies that the discharge-colour response time is also seasonally dependent.

Table 4.7 Pearson correlation (r) of colour (au m^{-1}) with rainfall and stage at optimum lagging.

(i) Rainfall (mm d^{-1})

	r	N	P
No lagging	0.2861	247	<0.001
Lagged by 6 ± 1 hours	0.3424	241	<0.001

(ii) Stage (units)

	r	N	P
No lagging	0.4474	199	<0.001
Lagged by 1 ± 1 hour	0.4739	198	<0.001

The correlation coefficients indicate that of the variables measured, stage (discharge) has the greatest influence on colour. In a stepwise regression rainfall was not entered into the equation due to its highly significant correlation with stage ($r=0.7443$, $N=199$, $P<0.001$). The change in stage between observations was significant but improved the degree of explained colour variance by less than 2%. The final colour-stage relationship has the form:

$$\text{Colour} = 0.21217 \log(\text{Stage}) + 0.6988 \quad r^2=0.5549,\ P<0.001$$

Repeating the analysis using rainfall and stage data lagged to the point of optimum correlation with colour gives the equation:

$$\text{Colour} = 0.21947 \log(\text{Stage}_{\text{lag 1hr}}) + 0.6965 \quad r^2=0.5855,\ P<0.001$$

Despite earlier reservations regarding the comparison of colour with dissolved organic matter, it is apparent that colour and DOM have very similar hydrological responses. A moderate positive relationship between DOM and discharge has been reported by Fisher and Likens (1972), while strongly positive relationships were found by Foster and Grieve (1982) and Grieve (1984) employing an eight hour sampling interval. The poor correlations found by Hobbie and likens (1973) and Arnett (1978) are thought to reflect the very low sampling frequencies they employed. Colour also has a strong positive relationship with discharge, and, like DOM, this relationship is improved when a higher sampling frequency is employed (How Stean-In Moor outfall,

daily sampling, r=0.2685; Armathwaite Gill, eight or one hourly sampling, r=0.4474).

The gradient (m) of the colour-stage regression gives information on the rate of colour removal from the catchment. The gradient is higher than that found for DOM and discharge by Fisher and Likens (op. cit.; m=0.137) and Grieve (1982; m=0.215) for forest catchments. If discharge had been determined using a rating curve, not simply stage height, a still higher gradient would result. This high colour-stage gradient is thought to be a consequence of the greater proportion of organic matter, as peat, in the catchment. However a high DOM-discharge gradient has been observed for a moorland stream draining a small peat catchment in Scotland (Grieve, 1984; m=0.37) and suggests that colour and DOM are strongly associated.

Grieve (1984) observed that DOM lagged approximately one hour behind discharge. This is comparable to the lagtime for colour observed in the this analysis. He also observed a clear seasonal distribution and autumn maxima in DOM, and that the ability to predict DOM from discharge varied temporally. This temporal variation in the DOM-discharge relationship has been attributed to seasonal variations in lag-time. Long delays of colour (absorbance at 425 μm) behind discharge have been noted for the South Tyne river draining peat uplands (Glover and Johnson, 1974). Lag times, believed to apply to any solute, have been observed for small (140-254 ha) catchments and were inversely

related to antecedent catchment moisture status, with longest lag times during dry summer conditions (Walling and Foster, 1975). These studies imply that colour is likely to be related not only to discharge, but to catchment soil moisture deficit.

It is apparent that DOM and colour have similar hydrological responses. Both exhibit a seasonal pattern with an autumn maxima and summer minima, both have strong positive correlations with discharge, and experience similar lag times. It has also been demonstrated (Chapter two) that the material responsible for discolouring water has a significant organic component, although not all the organics produce colour. These observations suggest that colour effectively consists of DOM, a product of organic matter decomposition. Decompositional activity is greatest during the warm dry summer, whilst the output of decomposition products is associated with stream discharge and therefore catchment flushing.

4.5 Temporal distribution of colour at field plot scale

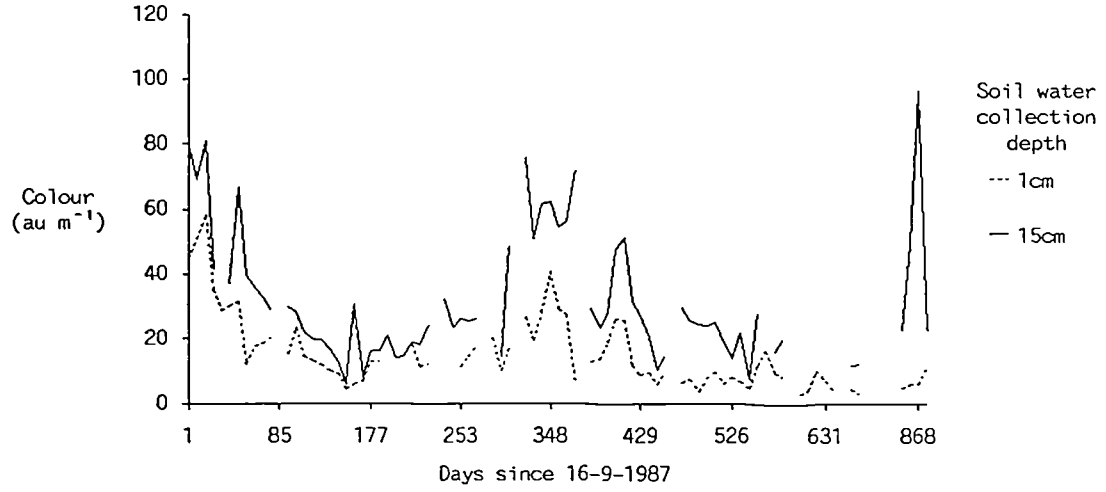
The temporal distribution of runoff colour has been described above, and related to local climatic variables. In this section an analysis of the temporal distribution of surface and near surface water colour is presented. This is done at the smallest scale studied, a peat throughflow pit.

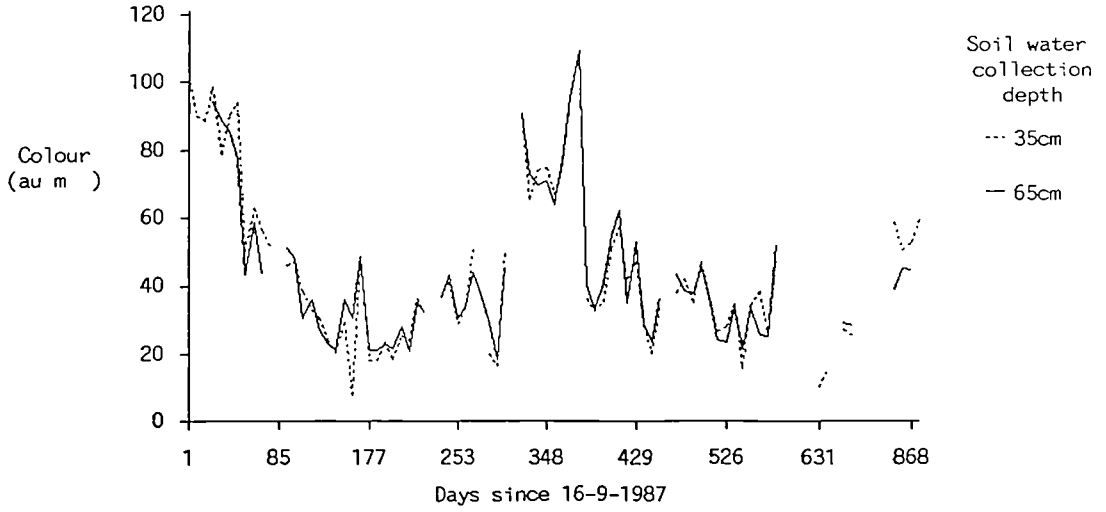
The throughflow pit is located in an area of Winter Hill (1011b) peat moorland on the How Stean catchwater (SE 065

765) which drains into Scar House reservoir via the How Stean-In Moor outfall. Water samples were caught by plastic sheeting inserted into a 1.5 m wide face at depths of 1, 15, 35 and 65 cm. These samples were diverted to one litre bottles which are emptied approximately weekly. A record of daily rainfall, measured within 500 m of the site was available. Total rainfall and mean daily rainfall between sampling visits was calculated. Soil moisture determinations at 10 cm intervals were made by neutron probe analysis. The moisture volume fraction (MVF) is determined from the slow neutron count rate by means of a calibration curve. Winter Hill peat is relatively rich in iron and is increasingly less acidic with depth. These factors influence fast neutron collisions and warrant a calibration specifically for Winter Hill peat. However, confidence in this calibration was low and the MVF was therefore determined using the calibration recommended by the manufacturers (Institute of Hydrology, 1981). The throughflow pit was monitored over a period of 156 weeks, beginning in September 1987.

The temporal distribution of colour is shown in figure 4.5. A clear seasonal pattern is again evident, with peak colour at all four layers occurring in late September to early October, and minimum colour in April. Descriptive statistics, by layer, are presented in table 4.8. The mean colour value (C_p) is the product of the mean colour and mean volume of sample collected at each layer. In some cases sample bottles had overflowed, leading to an

Figure 4.5 Temporal variation in soil water colour for a peat throughflow pit





underestimate of sample volume. The adjusted mean colour (C_a) assumes that, on average, samples that overflowed did so by 500 ml.

Table 4.8 Water colour (au m^{-1}) from Scar House throughflow pit, Sep 1987-Sep 1990

Depth (cm)	Mean(C)	σ	Min	Max	Mean(C_p) (au m^{-1})	Adjusted Mean(C_a) (au m^{-1})
0- 1	14.7	11.0	0.4	58.1	8.8	10.1
1-15	31.0	19.7	6.0	90.5	20.7	21.5
15-35	43.3	23.2	8.0	94.1	23.6	23.6
35-65	43.2	21.8	11.0	109.5	23.2	24.7

Surface water (0-1 cm depth) is significantly less coloured than sub surface water ($t=8.475, df=71, P<0.001$). This difference in colour may be due to the contact time between water and peat. Surface water samples will consist of water, including overland flow that have had the minimum peat-water contact time, and therefore the minimum opportunity for colour to be imparted. The time of travel of precipitation since falling on the catchment to its emergence at the catchment mouth is highly dependent upon the hydraulic pathways taken. Water that travels ostensibly as overland flow will be of low colour, with a relatively short travel time. Waters that infiltrate deeper into the peat profile will have a considerably longer time of travel to the catchment mouth, but will be significantly more coloured. This suggests that the time taken for colour to respond to precipitation is dependent on the hydraulic

pathways taken, and on antecedent conditions. This is likely to account for lag times observed between rainfall and colour, and discharge and colour in stream water. However, surface water samples are still significantly coloured, with as much as 40% of the colour of sub-surface samples. This may explain the apparent absence of any dilution effect prior to a storm hydrograph.

The relationships between colour and rainfall and colour and soil moisture were determined. Soil moisture at each sample collection layer was defined as the mean of all soil moisture determinations between that layer and the one immediately above (MVF_x). The change in MVF_x at each layer, between site visits was also calculated (δMVF_x). Colour was correlated with only one variable, MVF_x ($r=0.5693$, $N=298$, $P<0.001$), indicating that colour is imparted to throughflow as peat moisture content increases. When entered into a stepwise regression equation MVF_x is entered as the most significant variable, accounting for 32.4% of the variation in colour of all samples. The only other significant variable entered was rainfall on the day prior to sample collection, but this only added 2.42% to the total explained variance. Lagging colour data by up to four weeks did not improve the degree of explained variance.

The data describing the change in soil moisture at each layer, between site visits (δMVF_x) was divided into two sets; increasing and decreasing soil moisture. No correlation is found with colour for decreasing soil

moisture. However, there is a correlation between increasing soil moisture ($\delta MVF_x \geq 0$) and colour ($r=0.2577$, $N=94$, $P<0.01$). This indicates that colour is imparted to water on passage through the soil profile, and that a flushing effect operates. This further implies that colour accumulates during periods of soil moisture deficit when water movement is not sufficient to move it out of the profile.

4.6 Seasonal complexation of colour and iron

In chapter three the relationship between colour and iron in water was investigated. Iron was found to have a common source of origin with colour, and evidence was presented for the inclusion of iron in the structure of the colour producing material. This is significant in terms of colour production as it has been demonstrated that iron can increase the colour producing properties of dissolved organic matter (Lamar, 1968; Pennanen, 1972; Pennanen and Frisk, 1984; Heikkinen, 1984). There are strong parallels between DOM-Fe and colour-Fe. The correlation of colour and iron in water for all samples collected from the Upper Burn valley was highly significant ($r=0.8889$, $N=658$, $P<0.001$). This relationship was arrived at after lumping all colour and iron data collected throughout the year. In this section, the data is sub-divided according to collection date and analysed by correlation and regression. Results are presented in table 4.9.

Table 4.9. Seasonal distribution of colour and iron complexation in the Upper Burn during 1989, according to colour-iron regression analysis.

Date	N	gradient	constant	r	r^2
14 Jan	24	0.764	1.095	**0.8960**	0.8028
22 Jan	27	0.969	1.055	**0.9106**	0.8293
29 Jan	28	0.674	0.913	**0.8622**	0.7434
4 Feb	34	0.528	1.015	**0.8578**	0.7358
11 Feb	41	0.568	0.960	**0.8344**	0.6963
19 Feb	42	0.579	1.053	**0.8216**	0.6750
4 Mar	44	0.529	1.128	**0.8543**	0.7298
12 Mar	45	0.435	1.098	**0.6468**	0.4183
13 May	37	0.421	0.822	**0.7002**	0.4902
6 Jun	40	0.524	0.879	**0.6229**	0.3881
20 Aug	34	1.398	1.189	**0.8204**	0.6731
15 Oct	31	0.368	0.730	**0.8272**	0.6843
29 Oct	46	0.509	1.084	**0.8725**	0.7613
12 Nov	47	0.494	0.949	**0.8705**	0.7577

P-ANOVA of all regressions < 0.0001 **$P < 0.001$**

During 1989, fourteen 'snapshot' samples were taken in the Upper Burn valley, with up to fifty samples collected on each occasion. The timing of these 'snapshots' was deliberately biased towards autumn and winter when discolouration is greatest. However, despite this bias it is possible to see a seasonal component in iron-colour complexation. The coefficient of determination (r^2) is

high during autumn and winter, but falls to approximately half this value during the summer (figure 4.6). All coefficients of determination are significant ($P < 0.001$). This pattern indicates a very strong association between colour and iron during the autumn-winter, and a weaker relationship during the summer. This seasonality in colour-iron complexation was thought to relate to either annual patterns of precipitation or temperature.

There was no obvious pattern between the coefficient of variation and the rainfall distribution during 1989 (figure 4.6). No significant correlations were found between the r^2 value and the rainfall total on the day of sampling, the previous day, or total seven, fourteen and thirty day rainfall prior to sampling. The seasonality in colour-iron complexation may however be a product of temperature. Soil temperature is a critical factor determining the activity of soil micro-organisms. These organisms are highly significant in determining rates of organic matter decomposition. Iron availability may also be affected by microbiological processes. Heikkinen (1991) shows that total bacterioplankton density in the River Kiiminkijoki, Finland, greatly depends on temperature and iron concentration in runoff, and believed iron bacteria to be important in iron-organic complexation.

The colour-iron relationship was determined for water collected from a throughflow pit similar to that described in section 4.4, results are presented in table 4.10.

Figure 4.6 Seasonal variation in coefficient of determination (r^2) for colour-iron, Upper Burn valley, 1989

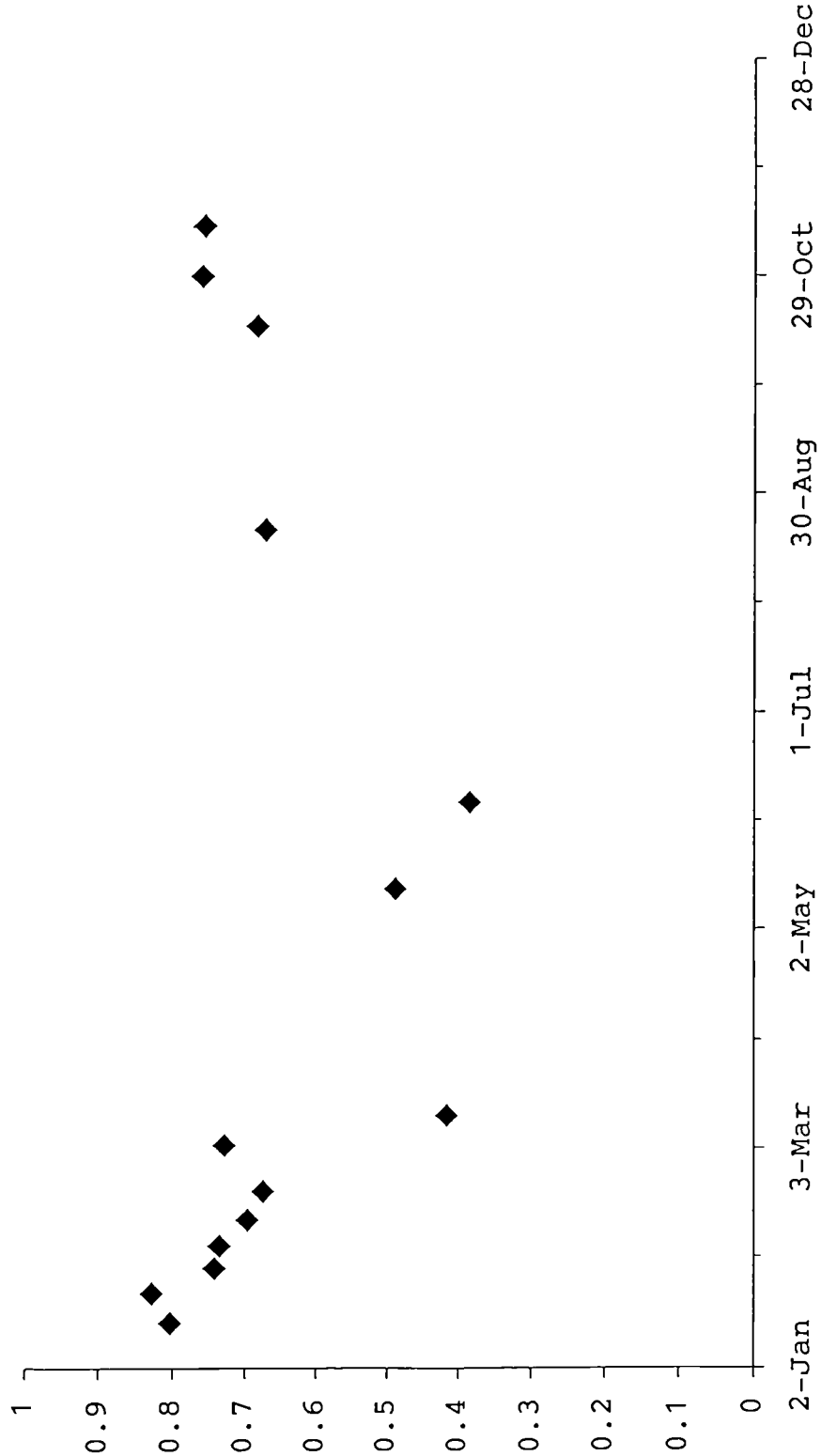


Table 4.10 Pearson correlation of colour (au m^{-1}), iron, pH and soil moisture for a peat throughflow pit.

	Colour	pH	MVF_x
pH	-0.2541		
	(N=163, P<0.001)		
MVF_x	0.4144	-0.2603	
	(N=195, P<0.001)	(N=135, P<0.01)	
Fe	0.9036	-0.6060	0.3020
	(N=70, P<0.001)	(N=38, P<0.01)	(N=52, P<0.05)

These results are consistent with those presented earlier and indicate that colour is acidic in nature, and is flushed from the throughflow pit during periods of high soil moisture. The relationship between iron and colour is particularly strong and is further evidence that iron is incorporated in the structure of the colour producing material. Iron is also positively correlated with soil moisture, although this may be complicated by iron interference in soil moisture determination.

These results suggest a rôle for iron in colour production. In an aerobic environment iron exists as iron (III) oxide, while in anaerobic reducing conditions it exists in the ferrous state iron (II) oxide. The salts of iron (II) oxide are characteristically green while those of iron (III) oxide are yellow-brown. These salts are formed in the reaction between iron oxides and acids. These acids may be organic, such as humic and fulvic acid. During summer more iron in runoff is in the reduced state, as water has a high

baseflow component. Following water table rise iron (III) oxide is flushed from peat and becomes the dominant form of iron in water. Therefore during the summer a low correlation exists between colour and iron, as most iron exists as ferrous salts. However, in the autumn and winter a high colour-iron correlation exists as the ferric yellow-brown iron salt is dominant. The population growth and activity of iron oxidising bacteria, such as Thiobacillus Ferroxidans may thus be significant in water discolouration processes.

4.7 The impact of catchment characteristics on the temporal distribution of colour

Chapter three demonstrated that the spatial distribution in mean catchment colour is determined by catchment characteristics. The dominant characteristics were those describing the areal extent of peat coverage, catchment slope and drainage. It was also demonstrated that for a series of forty six major Yorkshire catchments the variation in catchment colour (defined as colour range, standard deviation) was determined by the distribution of peat, rainfall and by drainage intensity (section 3.2). High colour events, those periods with colour ≥ one standard deviation above the mean annual colour, were also positively correlated with the areal extent of Winter Hill peat. Thus at the regional scale, the temporal variation in colour is significantly influenced by catchment characteristics.

The variability in water colour at a smaller scale, the Upper Burn and Upper Nidd valleys, was examined in a similar manner to the regional analysis. Water colour variability was defined by the standard deviation in annual sub-catchment colour ($colour_{\delta}$). Analysis at this reduced scale has the advantage of controlling for much of the spatial variation in climate. For example, Water Authority archives indicate that there are only minor variations in the spatial distribution of rainfall in the Upper Nidd valley.

No relationships between $colour_{\delta}$ and catchment characteristics were found for the Upper Nidd valley. This is largely attributed to the small sample size; fifteen sub-catchments along the How Stean catchwater. However, significant relationships were found for the adjacent Upper Burn valley (table 4.11) where the forty-five sub-catchments studied constitute a more satisfactory sample size.

Table 4.11 Pearson correlations (r) between $colour_{\delta}$ and sub-catchment characteristics of the Upper Burn.

	$Colour_{\delta}$		$Colour_{\delta}$
%1011b	0.6230	$Plat_5oct$	0.4346
Maxelev	0.5361	$\%Plat_5oct$	0.4124
Minelev	0.4375	$Plat_3oct$	0.4020
No3ord	0.5442	$\%Plat_3oct$	0.3752

$P < 0.001$, $P < 0.01$

When a stepwise regression equation is built the variable first entered is $Plat_{5}oct$. This variable, describing the distribution of well drained plateau areas accounts for 46% of the variation in $colour_{6}$. Variables describing catchment elevation are next entered accounting for a total of 58% of the total variation. However, all variables entered into this equation are highly correlated ($P<0.001$) with %1011b (Winter Hill peat). These variables are autocorrelated with %1011b and were excluded from a new stepwise regression:-

Step	Variable entered	r^2	P < ANOVA
1	%1011b	0.3312	0.0041
2	MSslope	0.5764	0.0020
3	StFreq	0.7106	<0.0001

The significant variables are those describing the catchment coverage by Winter Hill peat, and those describing catchment drainage (Main stream slope and stream frequency). This demonstrates that colour variability in the Upper Burn sub-catchments is consistent with the observed variability in colour at the regional scale. The influence of peat distribution on the colour response to rainfall in the three major sub-catchment groups draining the Upper Burn valley is seen in figure 4.7. The Colsterdale group, which has significantly more peat than the other groups, produces the most coloured water with the greatest variability. This is consistent with observations in 4.3 above, where higher gradients were noted for DOM-discharge relationships for peat catchments than for afforested catchments. A higher gradient implies more DOM

is lost per unit of flow, especially at high flow, given the exponential relationship. Colour is thought to be strongly associated with DOM.

An efficient drainage network may promote colour flushes in two ways. By lowering the water table, efficient drainage would result in a significantly greater zone of aerobic decomposition. In peat, this would increase the available colour store. Secondly, a high drainage density allows more rapid movement of drainage water, a faster export of organic solutes, and a more intense colour flush. Thus the temporal distribution of colour is a product not only of climate but is inextricably linked with a catchments' pedology, morphology and topography.

4.8 Conclusion

The temporal distribution of discoloured water is a product of climate and catchment characteristics. The long term annual pattern of water colour is highly regular, with colour peaking in the autumn, and at a minimum during the summer. Large variations in annual average colours are apparent. A significant upward trend in water colour towards the end of the 1970's is associated with the drought of 1976. However, the possibility of colour displaying periodicity in cycles considerably greater than one year, perhaps driven by astronomical phenomena, cannot be excluded.

The temporal distribution of colour is much less regular,

less predictable and more variable over shorter time spans. Analysis of changes in water colour at sampling frequencies ranging from daily to hourly indicate that colour is strongly related to discharge status. Colour is flushed from catchments during periods of high discharge, although this colour-discharge relationship is thought to vary seasonally dependent upon soil moisture status. Soil moisture status is influenced by rainfall and evapotranspiration rates, which have a greater relative importance in the water balance when applied to plateau areas. Plateau areas are the main colour sources. When catchments are below field capacity the movement of water and therefore colour out of the catchment is greatly reduced. It is during these periods of soil moisture deficit that organic matter decomposition increases and a store of soluble decomposition products accumulates. These products impart colour to water. The colour producing properties of these decomposition products may be altered by the availability of iron. A seasonal component in colour-iron complexation is evident, and it is suggested that this is a product of temperature dependent soil processes, particularly microbiological activity and possibly iron bacteria.

The intensity of colour flushes is positively related to the catchment characteristics of slope, drainage and extent of peat coverage. These factors control the potential for water to come into contact with discolouring material and for it to pass through the catchment quickly, contributing

to an intense colour flush. Thus the temporal distribution of colour is a product of a regulatory climate, modified by characteristics of individual catchments.

5. CONTROLLED INVESTIGATIONS ON THE GENERATION AND RELEASE OF COLOUR FROM WINTER HILL PEAT

5.1 Introduction and objective

Chapter three demonstrated the importance of organic rich soil deposits as sources of colour within catchments. The Winter Hill soil series, thick, acid blanket peat, was shown to be the single most dominant factor affecting the spatial distribution of coloured runoff for several major catchments in the UK uplands. Chapter three also indicated that variations in the colour of runoff from peatlands is related to the moisture status of the peat. Those catchment areas that are well drained, burnt or gripped for moorland management have elevated colour levels. McDonald et al (1990) have also found that colour levels are higher in streams draining predominantly south facing catchments. Analysis of the temporal distribution of colour, presented in chapter four, has shown that a strong seasonal variation exists. Highest colours are observed during autumn and lowest colours during summer. Water quality archives for the southern Pennines exhibit record autumn flush colour values following the severe drought year of 1976. Analysis of storm event data for selected catchments in the Upper Nidd has shown that colour is highly associated with rainfall and discharge, while analysis of near surface ground water shows that colour increases in response to elevated soil moisture status. These observations suggest that colour is produced during periods of soil moisture deficit, and removed following

soil moisture replenishment.

This chapter aims to qualify the process by which a store of colour producing material is generated in an organic soil and subsequently removed imparting colour to water. This generation and removal of colour is investigated by a series of controlled experiments with Winter Hill peat, previously identified as the major non-point source of colour in upland waters. Attention is focussed on drying and rewetting of peat and on the influence of peat and water pH on colour solubility.

5.2 Colour extraction from peats

5.2.1 Colour extraction at varied peat-water ratios

Observations on the spatial distribution of colour demonstrate that areas of Winter Hill peat with slopes $\leq 5°$ are major sources of colour within catchments. The spatial distribution of colour was found to be highly variable even within subcatchments of area ≤ 2.5 km^2. At this small sub-catchment scale high colours were found to originate from areas of low slope and from riparian Juncus swards which acted as effective peat traps. These observations suggest that water colour was enhanced in areas experiencing low hydraulic conductivities and minimal gravity drainage.

These observations were tested by monitoring the change in water colour in peat-water solutions over a 30 day period.

A Scar House peat sample was completely homogenised by blender, and divided into 0.5 g, 5.0 g and 50 g sub-samples. These sub-samples were then each mixed into one litre of distilled water. There were three replicates at each weight category. Periodically each vessel was gently stirred to completely mix the solution. Selected water quality parameters are presented in table 5.1, Colour change over the experimental period is illustrated in figure 5.1.

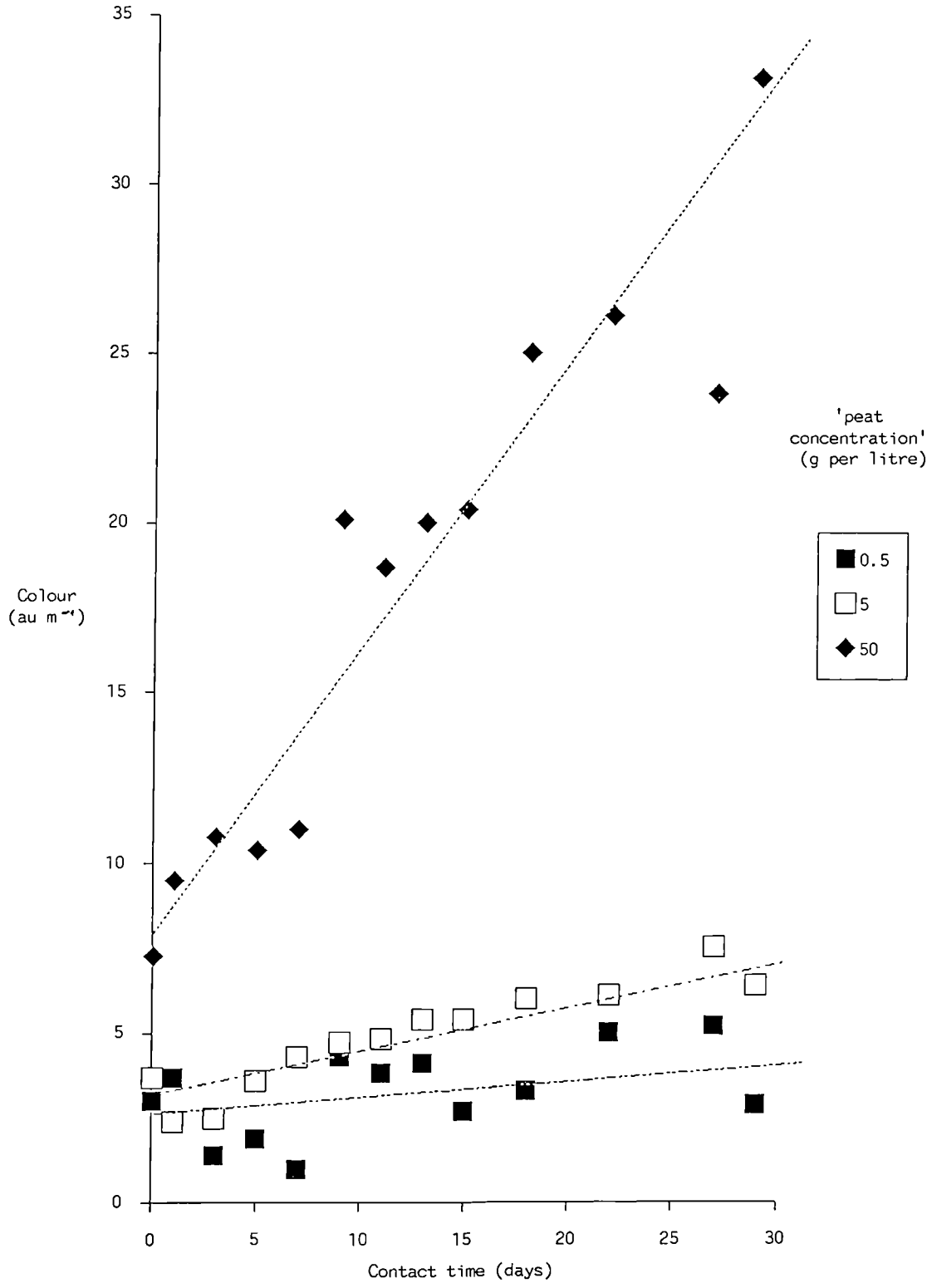
Table 5.1. Selected water quality parameters following thirty day peat saturation.

Initial peat concentration ($g\ l^{-1}$)	Solution pH	Solution turbidity (NTU)	Dissolved oxygen (%) saturation	Solution colour ($au\ m^{-1}$)
0.00 *	5.00	0.10	98.00	0.2
0.50	4.05	1.46	96.68	2.9
5.00	3.47	4.67	93.68	6.4
50.00	3.19	17.67	40.00	33.1

* Distilled water only

These results demonstrate that the release of colour from peat into water is dependent upon the peat-water contact period, and the initial peat volume. It is not thought that these colour differentials result from change in pH dependent solubilities as the solutions become more acidic as they become more coloured. It was demonstrated in chapter two that acidification of discoloured water results in a colour reduction. The increase in solution acidity is

Figure 5.1 Colour released to solution at varied peat-water ratios.



attributed to the release of colour producing organic acids. The reduction in dissolved oxygen content with increased peat concentration is attributed to chemical or biological oxygen demand associated with decompositional processes.

The colour differentials are thought to result from slow changes within the humic macromolecules. These humics are super abundant in peat soils. Humic molecules are thought to contain polar groups orientated towards each other, either to facilitate hydrogen bonding or coordination with inorganic cations. This orientation causes the molecule to shrink, and bind lower molecular weight fractions within the structure. These fractions are readily soluble in water and produce colour. However, when these humic substances are wetted they eventually swell, reducing the number of binding sites for the lower molecular weight fractions, which then pass into solution, colouring it. This process can take some time, as in the shrunk state, these macromolecules are hydrophobic, and so will prevent the penetration of water into their structure, and access to other macromolecules within a ped (Hayes, 1988). This may explain why a hundred fold increase in peat weight only results in a ten fold increase in colour.

These experimental observations are consistent with the field observations detailed above. Plateau and marsh areas have minimal gravity drainage promoting frequent or continual saturation and waterlogging. In these areas water

has a greater opportunity to cause macromolecular swelling bringing coloured fractions into solution. The low hydraulic conductivity in these areas allows water to become highly coloured. However, the low hydraulic conductivity also implies a low discharge rate and therefore that the colour flux may be similar to areas with higher discharge but lower colour production.

These observations may account for the very high water colours experienced in areas subject to artificial ditching. There is no evidence that water can become 'saturated' with colour. Figure 5.1 shows that the increase in solution colour is roughly linear with time. Therefore, given sufficient time and organic material water can become highly coloured. Samples taken from a plateau area drained by Grouse Gill (SE 053 726) Upper Nidd, had a true colour in excess of 1000 au m^{-1} (Martin, pers. comm., 1989). These saturated plateau areas are likely to have a massive colour store. Only a small portion of this colour store is removed in runoff due to the low discharge rate. If however, such an area is subject to artificial drainage, discharge is greatly increased and the colour store is removed more rapidly. Thus drainage of plateau areas can markedly increase the colour flux.

5.2.2 Colour extraction activity rates

In chapter two it was demonstrated that changes in the pH of a water affect its colour intensity. The solubility of soil organic matter, thought to contribute to colour, is

also pH dependent. Low molecular weight fulvic acids are soluble in water at any pH, high molecular weight humic acids are soluble in water at high pH, while humins are insoluble in water (Aiken, 1985). The ability of peat to colour water was assessed over a wide pH range, and at a variety of temperatures.

Peat was collected from Scar House pasture (SE 068 762) Upper Nidd, and divided into 50 ±1 g sub-samples. These samples were then soaked for 48 hours in 250 mls of distilled water adjusted to a pH of between 1 and 10. Samples were then maintained at 20°C, 45°C, 65°C and 100°C, under reflux conditions for three hours. Supernatant colour was determined. Results are illustrated in figure 5.2.

The ability of peat to colour water is dependent upon solution pH. There is a general increase in supernatant colour throughout the pH range, with highest colours produced at high pH. This is consistent with the solubility properties of dissolved organic matter and suggests that the higher molecular weight, humic acid fractions are responsible for colour production. However, upland soils and water are naturally acidic, and under these conditions the high molecular weight organics are not likely to be responsible for discolouring water as they are less soluble in that pH environment. Therefore although humics have the potential to be the major colour producers, it is thought that the lower molecular weight fulvic acid fractions are mainly responsible for naturally occurring discolouration. A general increase in supernatant colour was observed with

Figure 5.2 Variation in colour extracted from peat at varied solution pH and temperature

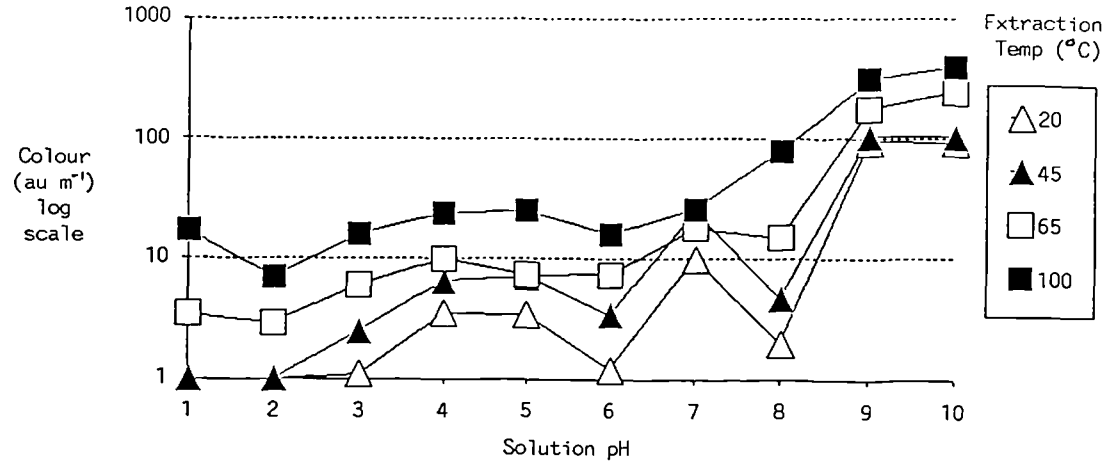
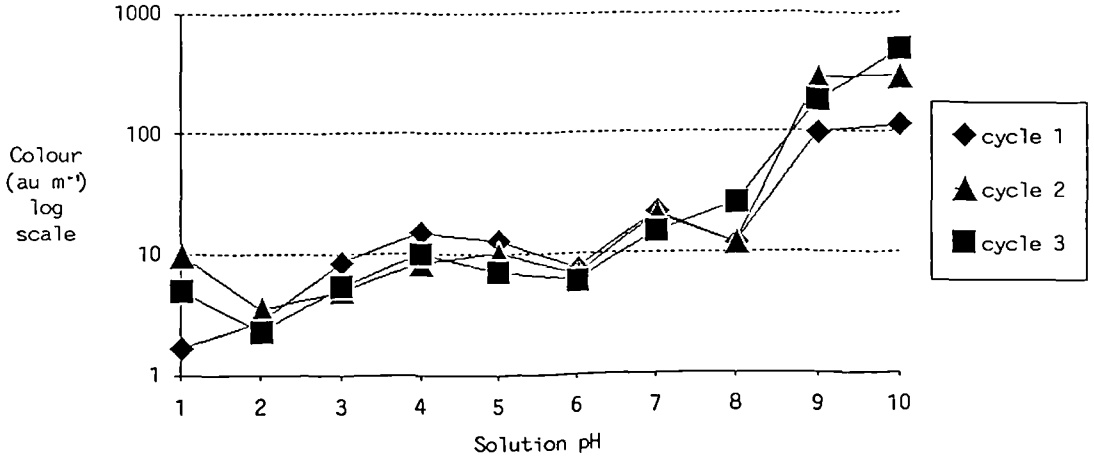


Figure 5.3 Variation in colour extracted from peat solution of pH 1-10 through three wet-dry cycles



increased solution pH, but significant peaks at pH 4-5, pH 7 and pH 9 were evident. These peaks may result from the action of biochemical processes within the peat, possibly enzyme activity. Enzymes, produced in this case by soil microorganisms, are known to have narrow pH bands at which they function most effectively (Sawyer and McCartey, 1978). Biochemical reaction rates generally follow Van't Hoffs rule of doubling for every 10°C rise in temperature over a restricted temperature range. This is usually expressed as the Q_{10} value, that is, the ratio of a reaction rate at a particular temperature to the rate 10°C lower. Values for Q_{10} across the pH range studied are presented in table 5.2.

Table 5.2. Colour extraction reaction rates.

Temp range (°C)	20-45	45-65	65-100
pH	Q_{10}	Q_{10}	Q_{10}
1	1.00	1.84	1.58
2	1.00	1.70	1.28
3	1.39	1.55	1.32
4	1.28	1.24	1.28
5	1.36	1.02	1.42
6	1.52	1.48	1.25
7	1.44	0.88	1.11
8	1.41	1.79	1.61
9	1.04	1.31	1.17
10	1.05	1.54	1.14

At low temperatures, 20°C and 45°C, reaction rates are greatest near neutrality. This is the pH range where the function of most enzymes is optimal, and suggests that enzymes are important in organic matter decomposition and colour production. The pH-colour relationship is consistent at 20°C and 45°C, but begins to breakdown at higher temperatures. This also suggests that there is a biological component to colour production as biological reactions are more likely to breakdown at temperatures in excess of 45°C than chemical reactions. The breakdown may be due to the process of denaturation, where enzymes are no longer able to function well at higher temperatures, or where microorganisms are no longer able to produce the relevant decomposing enzymes. It is thought that many enzymes may contribute to organic matter breakdown in peat and subsequent colour formation. Hydrolases, controlling hydrolytic reactions, are able to break down sugars, starches, cellulose and amino acids, producing degraded sugars, maltose, cellobiose, and organic acids respectively. Desmolases are able to rupture linkages that are not hydrolysable, and include enzymes involved in oxidation-reduction reactions. These observations imply that peat decomposition, and the production of organics capable of discolouring water is greatest during the summer. Elevated summer temperatures may increase biochemical decomposition reaction rates, but are not likely to reach or exceed the point of denaturation.

Elevated soil temperatures during summer are generally

associated with reduced soil moisture content. The effect of soil moisture reductions on supernatant colour was assessed. The colour extraction procedure detailed above was repeated at 20°C, over the same pH range, 1-10. However, after the initial colour extraction the peat samples were allowed to air dry for seven days, before repeating the extraction procedure. Three air drying periods were employed, each followed by colour extraction. Results are presented in figure 5.3, and in table 5.3.

Table 5.3. Colour (au m^{-1}) of water extracted from Scar House peat in response to air drying.

Solution pH	Number of air dry periods			
	None	One	Two	Three
1	1.0	1.7	10.0	5.0
2	1.0	2.8	3.5	2.3
3	1.1	8.5	5.0	5.4
4	3.5	15.0	8.3	10.0
5	3.4	13.0	10.2	7.1
6	1.2	7.5	6.7	6.0
7	10.0	22.0	21.0	15.0
8	2.0	12.0	12.0	26.0
9	96.0	100.0	290.0	185.0
10	94.0	115.0	295.0	500.0
Σcolour pH 1-10	213.2	297.5	661.7	761.8
Σcolour pH 1-7	21.2	70.5	64.7	50.8

The pattern of extract colour is very similar to the pattern presented in figure 5.2. Following air drying of peat, there is a general increase in colour with rising pH, but this increase is non-uniform. The rate of increase is greatest at pH 3, 6, and 8, which corresponds closely to the Q_{10} (20-45°C) values above. This indicates that the biologically orientated decomposition processes operate during periods of moisture reduction. However, these observations also demonstrate that air drying peat increases the store of water soluble colour across the full pH range studied. In all cases supernatant colour was greater after the first period of air drying, and in some cases increased after each air drying period. This demonstrates that the pool of colour producing organics is added to during the air drying period. If this were not so a gradual reduction in colour would be expected as the colour pool was depleted following repeated extraction. These observations indicate that colour is enhanced in response to drying, and that the maximum rate of colour increase takes place at optimum pH values. This suggests that colour is a product of organic matter decomposition, a biochemical process controlled by enzymes produced by soil microorganisms.

5.3 Colour output from prolonged peat leaching

The temporal distribution of colour was investigated in chapter four. Results of these investigations showed that colour has a clear seasonal distribution, with highest

colour flows commonly observed during autumn and early winter. Intensive sampling of runoff from small ($\leq$ 2.5 km^2) and medium ($\leq$ 30 km^2) sized peat covered catchments demonstrates that coloured flows are strongly associated with the timing and rate of rainfall and discharge. These observations suggested that colour was removed from upland catchments by a process of catchment flushing. Therefore, peat flushing and colour washout were studied under laboratory controlled rainfall and discharge regimes.

The apparatus used consisted of forty glass columns, each capable of holding one kilogramme of 'fresh' peat. Water is delivered to each column from a main overhead reservoir feeding eight smaller reservoirs. Each secondary reservoir has five tubes delivering water to individual glass columns. The secondary reservoirs can be moved vertically through 16 cm so as to produce varying hydrostatic heads and flow rates. Water is finally delivered to the peat samples via hypodermic needles which allows water to be added dropwise and further acts to regulate flow rates. Water flowing through the peat samples is funnelled into a collecting beaker below.

5.3.1 System calibration

It was necessary to calibrate the system in order to determine what 'rainfall' rates were achieved with different combinations of hydrostatic head and needle bore diameter, and to determine which combination gave the most consistent flows. Results are presented in figure 5.4(a-b).

Figure 5.4a Equipment calibration. Effect of needle bore and hydrostatic head on simulated rainfall rate.

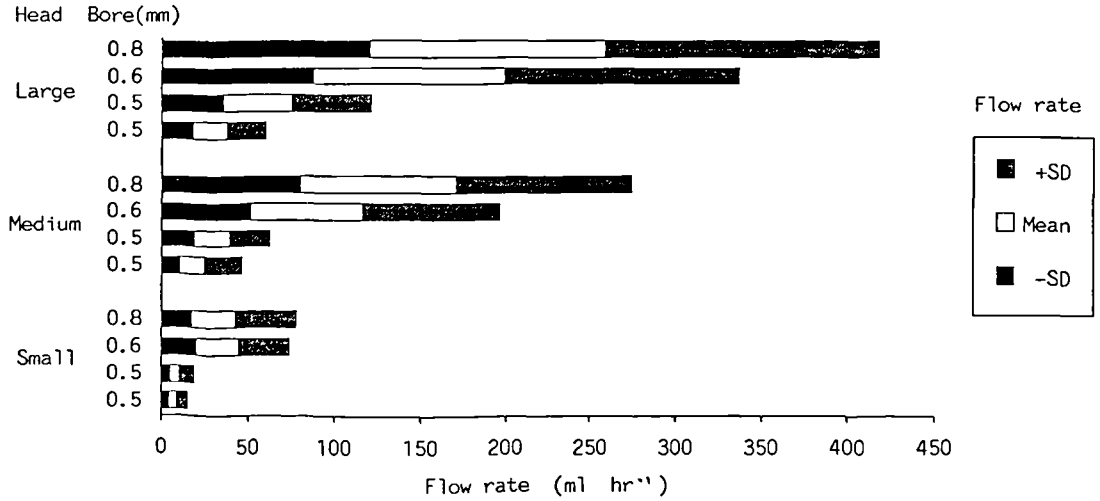
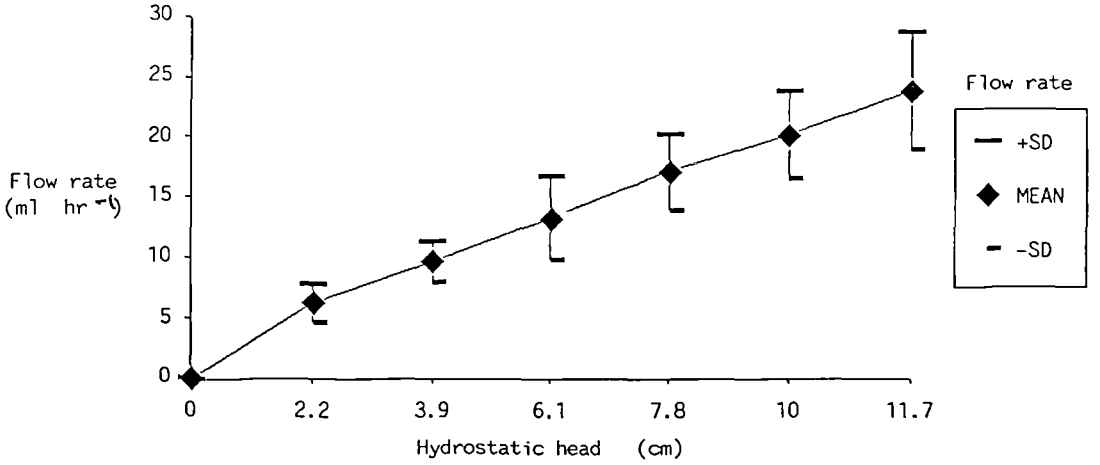


Figure 5.4b Equipment calibration: Variation in simulated rain rate with hydrostatic head using 0.5mm bore needle



Best results were achieved using the smallest needle bore available, 0.5 mm. This gave the most stable flow rates, and was capable of delivering as little as 6.3 ml hr^{-1}. All peats used in subsequent experiments were collected from Scar House pasture (SE 068 762) and used within 24 hours of collection. Peat samples (1000 ±5 g) were roughly homogenised by hand prior to use and firmly packed into the columns. Each treatment had a minimum of five replicates.

5.3.2 Response to varied 'rainfall' rates

The effect of 'rainfall' rate on elute discolouration was investigated. Six rainfall rates were studied, varying from 6.3 ml hr^{-1} to 23.95 ml hr^{-1}. Artificial rainfall was maintained for a twenty-four day period, with elute colour and volume measured every other day. Results are presented in figure 5.5. The general trend is one of colour reduction with prolonged rainfall, indicating a depletion of the colour store. Elute colour is dependent on the size of the initial colour store, and the flow rate through the peat. If it is assumed that the initial colour store is equal for all treatments, then colour reduction is proportional to flow rate. The area and length of all peat columns were equal, and it is assumed that at these high rainfall rates all peats became saturated, and had the same permeability. Therefore, from Darcy's law the rate of flow of water is proportional to the hydrostatic head, that is, the rainfall rate. Thus elute colour should be proportional to the rainfall rate. However, high rainfall is associated

Figure 5.5 Colour variation during prolonged peat leaching (au m^{-1})

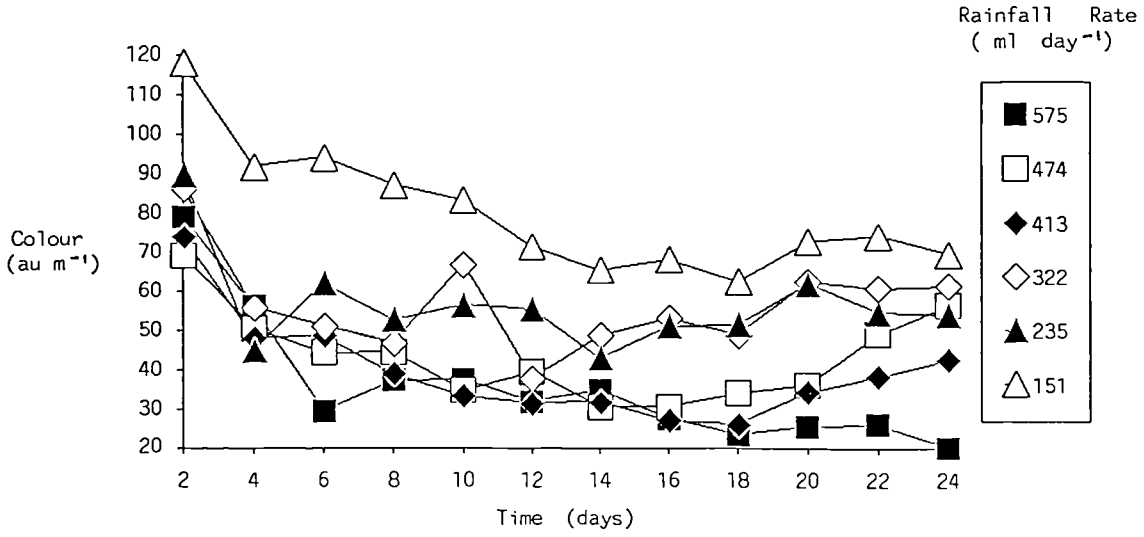
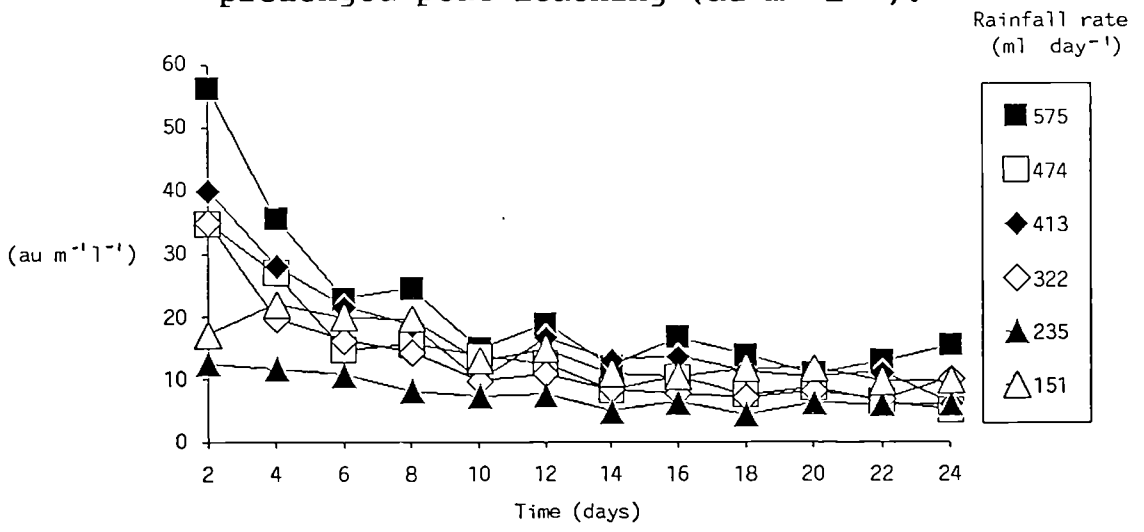


Figure 5.6 Colour variation during prolonged peat leaching (au m^{-1} l).



with low elute colour, and conversely low rainfall rates with high elute colour. This is a product not only of solute pick up, but of dilution too. Therefore to control for this dilution effect the colour flux should be considered, so colour is expressed as au m^{-1} l .

Figure 5.6 illustrates the effect of different rainfall rates on the colour flux. The general pattern is more clearly one of colour reduction with time, and is near to an exponential decay curve. The colour at any time may be represented by:

$$C_t = C_0 \, e^{-\alpha t}$$

Where C_t = colour at end of time t (au m^{-1} l)

C_0 = colour at start of period (au m^{-1} l)

α = coefficient of peat

e = base of natural logarithm

This function was fitted by eye to each of the colour flux plots in figure 5.6. For each of the six rainfall rates employed, the coefficient of peat (α) was calculated. Results are presented in table 5.4.

At the four highest rainfall rates there is close agreement between the value of α. This does not suggest that colour is independent of rainfall rate, as the colour flux (au m^{-1} l) is under study. It does demonstrates that the rate of colour removal in saturated peats is highly consistent, once the effect of rainfall rate has been controlled for.

Therefore the removal of colour from peat is dependent upon the rate of flow of water through that peat. For each peat column the total colour released (au m^{-1}) during the experimental period is very strongly related ($r=0.9994$, $N=30$, $P< 0.001$) to the quantity of water that has passed through it (figure 5.7). Therefore, under field conditions the rate of colour removal in saturated peat is directly proportional to the discharge rate through it, and confirms that a colour washout process operates.

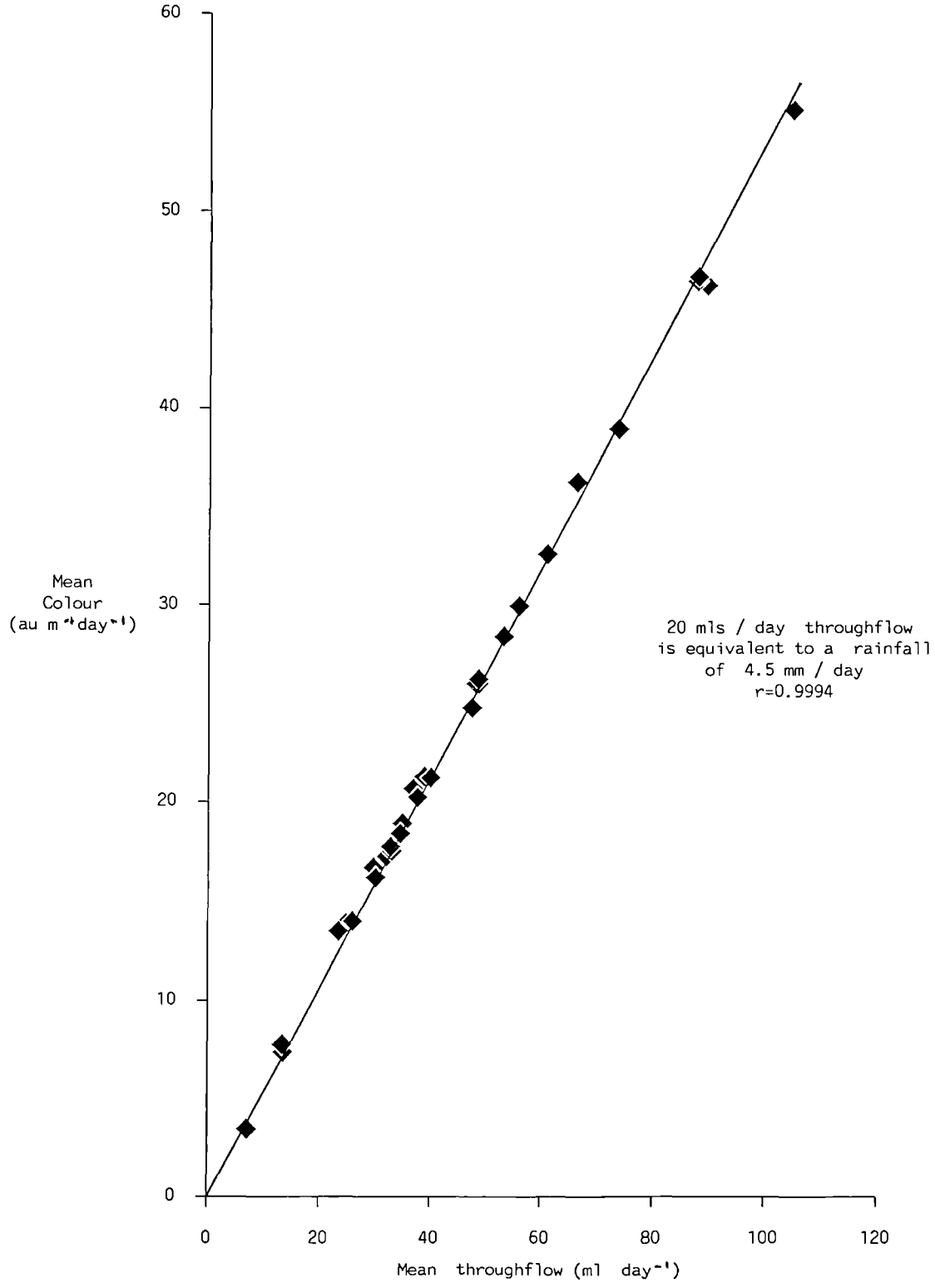
Table 5.4. Effect of rainfall rate on colour washout rate.

Rainfall rate mls hr^{-1}	mm d^{-1}	% long term average annual rainfall *	C_0	C_{24}	$-\alpha t$
23.95	130.3	238.0	56.4	12.4	1.51
19.75	107.4	196.2	34.9	6.4	1.69
17.20	93.6	170.9	40.1	8.7	1.52
13.40	72.8	132.9	35.1	6.7	1.65
9.80	53.3	97.4	15.0	5.3	1.04
6.30	34.3	62.6	26.1	10.0	0.96

* Long term (1941-1970) average annual rainfall at Scar House = 1314 mm

The lower coefficients of peat (α) at the two lower rainfall rates indicates that the colour store was not being depleted as quickly as at the high rainfall rates. This may indicate that these peats were not readily saturated, although these are still very high rainfall

Figure 5.7 Relationship betweeen elute colour and throughflow rate



rates compared to natural rates. Therefore, this may be an indication that the colour store is being replenished to some extent during the washout process.

5.3.3 Response to change in 'rainfall' rate

The discharge rate through a saturated peat determines the degree of water discolouration. Therefore it is anticipated that an increase in water flow through a saturated peat is coincident with an increase in colour. A control group, with ten replicates, was subject to a constant rainfall rate of 6.3 ml hr^{-1}. A treatment group, also with ten replicates, was subject to the same initial rainfall rate. This was later increased to a constant 23.95 ml hr^{-1} for a four day period. The colour response to increased artificial rainfall rate is illustrated in figure 5.8.

Both groups experience an initial 'first flush' phase, with colour levels falling from 20 to 5 au $m^{-1}l$ after fourteen days. The control group continues to experience a slow but steady decline consistent with the exponential decay observed earlier. Once the rainfall rate for the treatment group is increased a rapid rise in colour is seen, from 5-18 au $m^{-1}l$. Once the rainfall rate is returned to the control level, the colour output falls to match the control group. Thus an increase in rainfall rate produces a second colour flush almost equal to the intensity of the first. In both groups log colour is strongly related to flow rate through the peat (Control $r=0.6639$, $N=120$, $P<0.001$; Treatment $r=0.5286$, $N=120$, P

Figure 5.8a Response of elute colour to variation in throughflow rate.

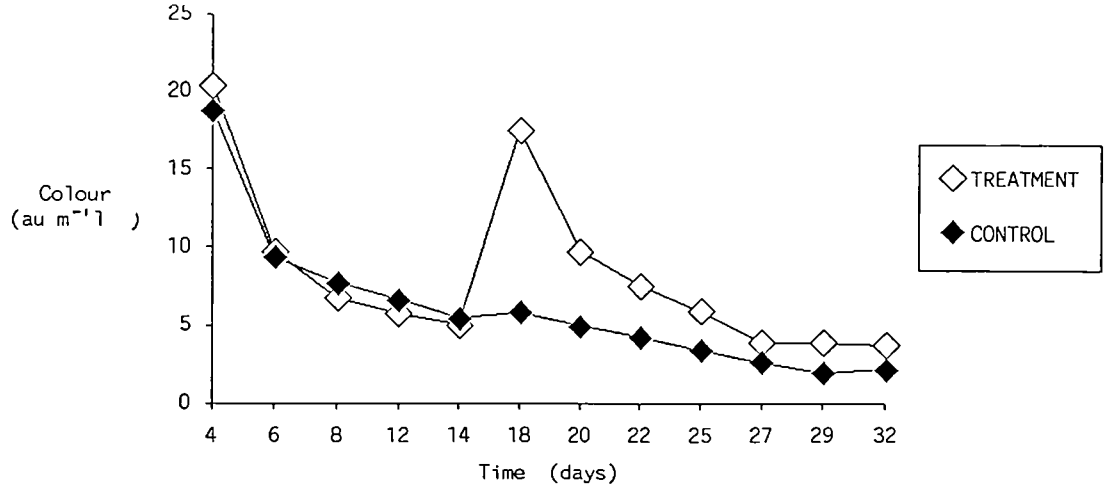
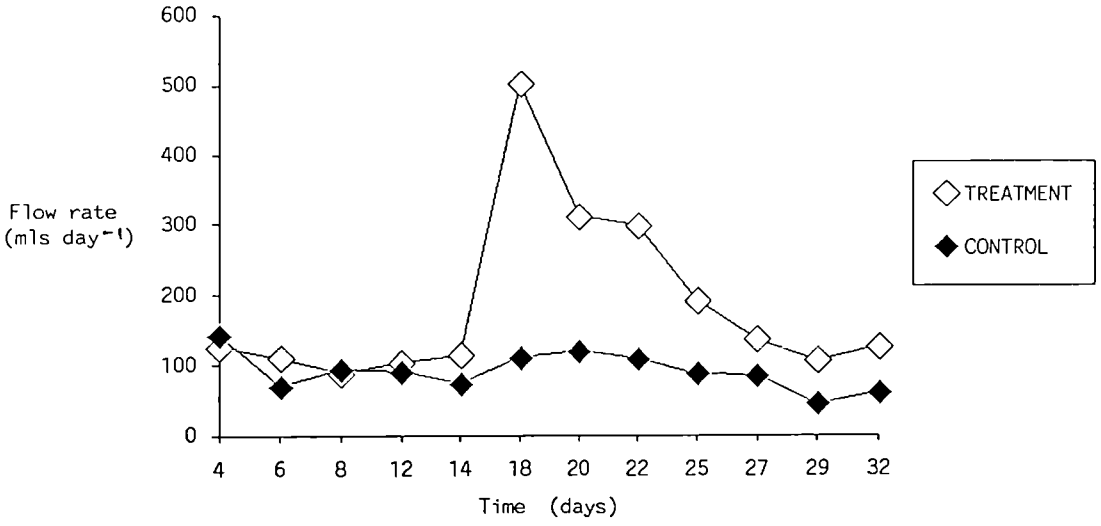


Figure 5.8b Variation in throughflow rate



<0.001).

Parallels can be drawn with catchment hydrological observations. In chapter four it was demonstrated that colour peaks in runoff were coincident with increased discharge following precipitation. A similar discharge-colour response is evident in controlled investigations. This demonstrates that the intensity of runoff colour following rainfall and elevated discharge is strongly associated with catchment flushing processes. Time lags between colour and discharge have been observed during storm hydrographs, but not during the controlled investigation. This is to be expected where peats are saturated and hydraulic pathways short.

5.3.4 Variation of peat soil moisture

Earlier controlled investigations indicated that reducing the moisture content of a peat increased the intensity of colour that could be extracted from it (section 5.2.1). It has also been shown for a peat throughflow pit that colour is related to soil moisture content (chapter 4). In addition, analysis of long term trends in colour indicates that colour does not decrease annually in accordance with the exponential function described above. Indeed annual average colour in some years is seen to increase significantly. Largest increases have followed particularly dry years, with highest recorded colours following the 'drought' years of 1976 and 1984, two of the driest years on record in the UK. Statistical analysis of long term

trends in water colour for the Upper Nidd valley (Naden and McDonald, 1989), demonstrates that more than 50 % of the variation in runoff colour can be accounted for by soil moisture deficits three and fourteen months previously. These observations suggest that colour increases are not merely related to increases in discharge and catchment flushing, but that soil moisture deficit contributes to the production of a 'colour store'.

The effect of drying peat on the colour of water flushed from it was investigated using the leaching apparatus described above. A control group of five peat columns was continually flushed for a 28 day period at 17.2 ml hr^{-1}. Four treatments, each with five replicates were used. Treatments were also subject to flushing at 17.2 ml hr^{-1} but were additionally subject to induced drying followed by renewed flushing. Three drying periods were induced, each of six days duration. Treatment groups were differentiated according to drying temperature; 17°C, 25°C, 37°C and 44°C. The initial gravimetric moisture content of all peats was 92.4%. The moisture losses following each drying period are shown in table 5.5.

The pattern of mean colour output from each group is illustrated in figure 5.9, and the change in colour following drying and re-flushing presented in table 5.6. Colour output from the control group exhibits a gradual decline throughout the flush period, consistent with the exponential decay observed earlier. However, almost without

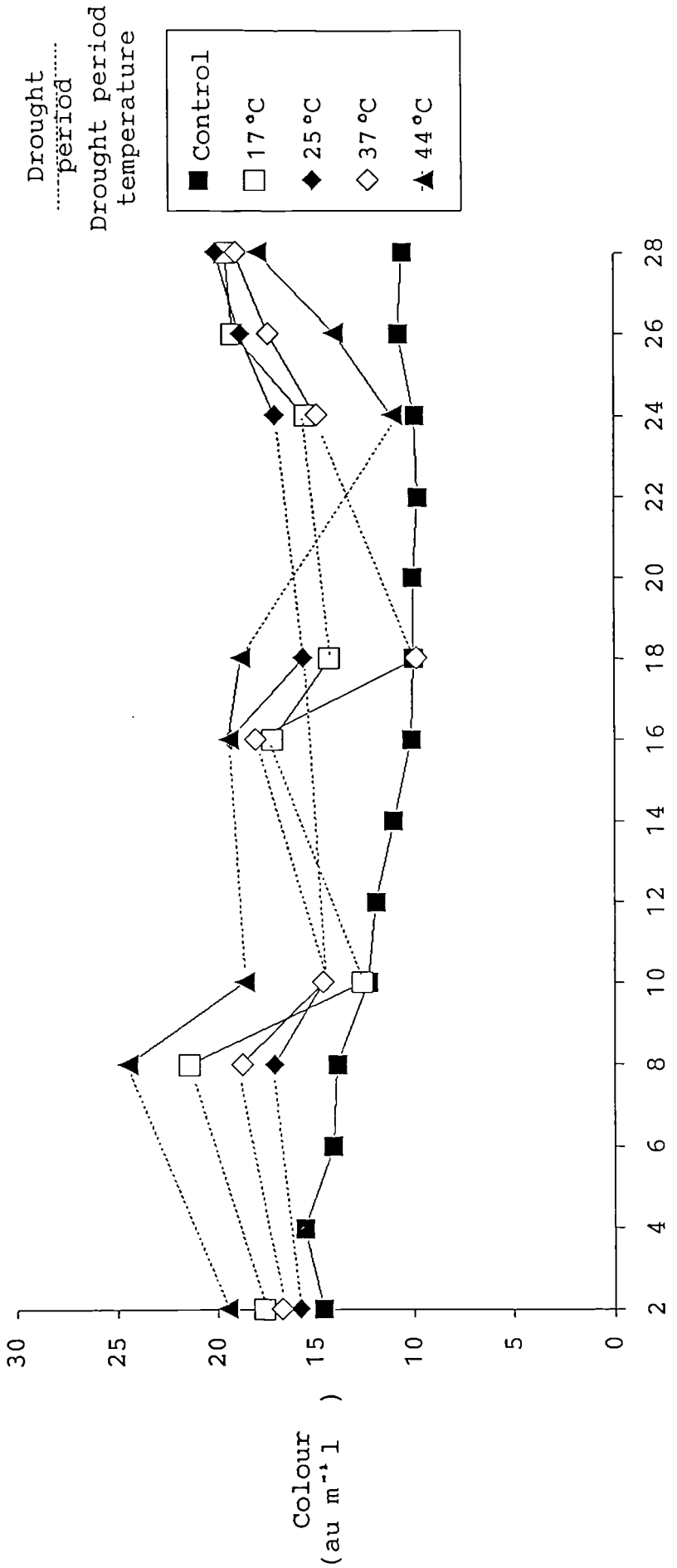


Figure 5.9 Impact of induced drought on elute colour during prolonged leaching

exception, colour during the re-flushing phase was higher than the pre-dry period colour. The total colour flux was significantly greater than control values for all treatment groups (eg. for colour flux nearest to control flux, 37°C; $t=2.668$, $df=39$, $P < 0.01$). This is a clear indication that drying has increased the available colour store.

Table 5.5. Peat moisture (%) following induced drying.

Drying temp (°C)	1st dry period	2nd dry period	3rd dry period	Final moisture (% original)
Control (17)	-	-	-	-
17	97.54	97.25	93.43	100.99
25	81.33	84.54	59.93	74.78
37	84.77	84.07	59.79	66.55
44	81.87	80.90	52.12	57.09

There is no consistent pattern between colour increase following each drying period and the drying temperature. This is attributed to modifications to the nature of the peat during the drying process. At 44°C, following the second and third drying periods, there are the only instances of a colour decrease. These are attributed to a reduction in hydraulic conductivity. The major moisture loss in this treatment group renders the peat less permeable to water, and so the opportunity for solute pick-up is reduced.

Table 5.6. Colour change (au $m^{-1}l$) following induced drying and re-flushing.

Drying temp°C	1st dry period	2nd dry period	3rd dry period	Σchange	Mean 28 day colour (au $m^{-1}l$)
Control(17)	-0.68	-2.17	-0.06	-2.91	11.80
17	3.85	4.59	1.21	9.65	17.21
25	1.29	4.69	1.42	7.41	17.35
37	2.02	3.42	5.10	10.55	16.23
44	4.97	0.83	-7.71	-1.91	18.04

The greatest total colour increase occurs in the 37°C treatment. This may indicate that coliform bacteria, whose optimum growth temperature is 37°C, are significant in colour production during drying periods. A colour increase is also seen in the 17°C treatment, which experiences a moisture loss of ≤ 7%. This suggests that in the absence of washout processes the colour store will continue to grow even when there is little or no drying. These observations imply that the generation of a colour store within a catchment will proceed as long as rainfall and wash out processes do not deplete it. Higher soil temperatures, such as those experienced during summer, will rapidly increase the size of this store. If excessive drying reduces the permeability of peat to water, then the colour cannot be released until the permeability is increased. These observations also indicate that temperature dependent soil microbiological processes may be significant in colour

production.

5.3.5 Variation in peat storage temperature

Observations on the seasonal pattern of colour, and of controlled experimentation indicate that the generation of colour may be a temperature dependent process. The treatment temperatures used in the study of induced drying were relatively high and are unlikely to persist under field conditions. Peat was divided into two treatment groups; one stored at 8°C equivalent to an autumn or mild winter soil temperature, and the other at 25°C, equivalent to a hot summer. After 36 days at these temperatures each treatment (five replicates) was flushed with water at a rate of 17.2 mls hr^{-1} at a temperature of 17°C-19°C for a further 18 days. Peat was enclosed in polythene in an attempt to reduce drying, but after storage the 25°C treatment was significantly drier ($t=10.56$, $df=4$, $P < 0.001$). Therefore the combined effects of temperature and drying are studied.

Results are illustrated in figure 5.10. It is difficult to draw conclusions about colour production due to the significant difference in drying. However, tentative conclusions can be drawn the pattern of colour output. Colour release from peats stored at 25°C was roughly approximate to an exponential decay. However peat stored at 8°C experienced a rise in colour on flushing, reaching a maximum after 8 days, after which colour levels declined gradually. This colour rise cannot be attributed

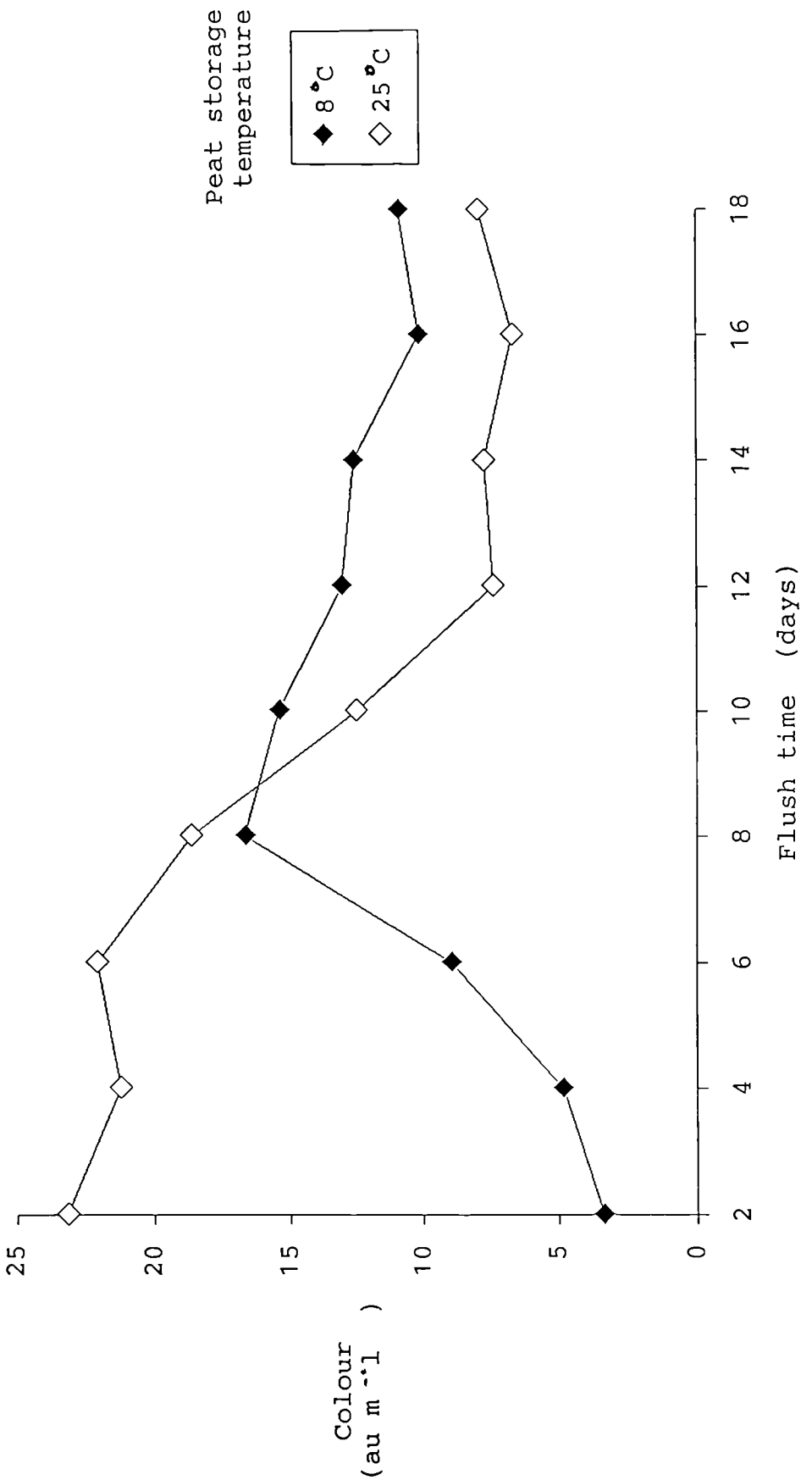


Figure 5.10 variation in elute colour following differential peat storage temperature

to a gradual increase in soil moisture and subsequent colour wash out, as the 8°C peats never lost more than 10 % moisture, indicating that their permeability was not radically altered. If such a process were to operate it should be more evident in the 25°C peats, and this is not so. This pattern of colour output suggests that the rate of colour production in the 8°C peats is low during storage, but once the temperature is increased colour production accelerates. This implies that colour production in peats is a year round process, but is very much greater during the summer when soil temperatures are higher. This is comparable to the seasonal pattern of soil microorganism activity.

5.4 Discolouration of water by peat following induced drought and rainfall simulation

Earlier investigations have indicated that soil moisture and soil moisture deficit are significant factors in water discolouration processes. Initial investigations were based on the analysis of water quality archives which may be complicated by other seasonal influences, such as temperature. Controlled experimentation has centred on artificially induced drying in relatively small highly disturbed peat samples. In this section, the impact on water colour of naturally induced soil moisture deficit in largely undisturbed peats is assessed.

5.4.1 Methodology

(a) Sample collection and storage

Thirteen peat samples were collected from the Scar House area of Upper Nidderdale, North Yorkshire (SE 06 60) and six from the Derwent Valley, Derbyshire (SK 20 90). Three of the Derwent valley samples were collected from areas of extensive erosion with little or no surface vegetation cover. All samples were taken from areas of Winter Hill peat, the soil association previously identified as the primary non-point source of water discolouring material. In order to minimise peat disturbance a 20 cm diameter steel ring was driven into the peat to a depth of 30 cm and then dug out with the intact peat core inside. The peat was then covered with thick circular wooden blocks to protect the surface and pushed from the steel ring by hand or using a screw type 'hub-puller'. The peat core was then firmly wrapped in plastic leaving only the surface exposed to the air. All cores were then stored under glass to exclude any precipitation whilst still being exposed to normal external air temperature and daily light-dark cycle. Cores were stored in this manner for up to 600 days. To ensure even drying from the surface only, cores were periodically rewrapped to accommodate peat shrinkage. The deviation in moisture content between the edge and centre of the core after 360 days storage was 1.7 % at 3 cm and 0.15 % at 23 cm depth. Each core was cut down to a standard length of 23 cm prior to rainfall simulation to remove any bottom peat that had suffered compression during

storage.

(b) Rainfall simulation

At the end of its allocated drought period each core was subjected to rainfall simulation. The simulator has a ten litre reservoir suspended above the core and is kept in gentle constant motion by attachment to an eccentric cam. The reservoir has 40 hypodermic syringes set into its base. Different needle sizes allow various drop sizes to be achieved, which, coupled with the hydrostatic head allows the rainfall rate to be controlled. A needle bore of 0.5 mm and an initial hydrostatic head of 15 cm results in a rainfall rate of 4.5 mm hr^{-1} falling to 2.8 mm hr^{-1} at the end of the 24 hour simulation period. This gives an equivalent daily rainfall rate in excess of 80 mm d^{-1} which, with reference to table 5.4 suggests that any colour production during peat rewetting should be minimal in relation to colour production during drying. Distilled water modified to pH 4.8-5.2 was used.

Each peat core is supported on a large funnel which directs the throughflow to a sample bottle. A 15 cm diameter ring is sealed onto the funnel and firmly pushed into the base of the peat core. This ensures that only water passing directly through the peat is collected. Water that does not pass through the ring is diverted through holes in the funnel above the ring to waste. Moisture content of the peat was determined gravimetrically at 0-3 cm, 3-9 cm, 9-15 cm and 15-23 cm depth intervals by sub-sampling 2 cm into

the core, before and after simulation. Water colour was measured after 0.45μm filtration on a Pye-Unicam UV/Vis spectrophotometer at 400 nm.

5.4.2 Results

The typical pattern of colour output during rainfall simulation is shown in figure 5.11. All peat samples show a rapid initial rise in colour, usually peaking after 4-6 hours, followed by a gradual decline. Water pH (see section 5.6) mirrors this pattern, with a rapid increase in acidity to the colour peak, followed by a gradual decline. This is consistent with the removal of colour producing dissolved organic matter, such as fulvic and humic acids, contributing to an 'acid flush'. Figure 5.11 also illustrates the apparent increase in colour with storage time. For each peat core, the total colour output during the 24 hour rainfall simulation period (TCO_{24}) was calculated as:

$$TCO_{24} = \Sigma (C_t \times T_t) \qquad (1)$$

Where C_t is water colour, T_t is throughflow in litres and t is time in hours. Two observations were omitted. Both of these had high standardised residuals (>2.0) whereas all other observations were typically at or below 1. The anomalies were in cases which had dried to a point where they shed water and did not begin to rewet within the 24 hour period relevant to this examination. Figure 5.12 shows the increased delay in colour response as drought severity

Figure 5.11 Elute colour from droughted peat during rainfall simulation

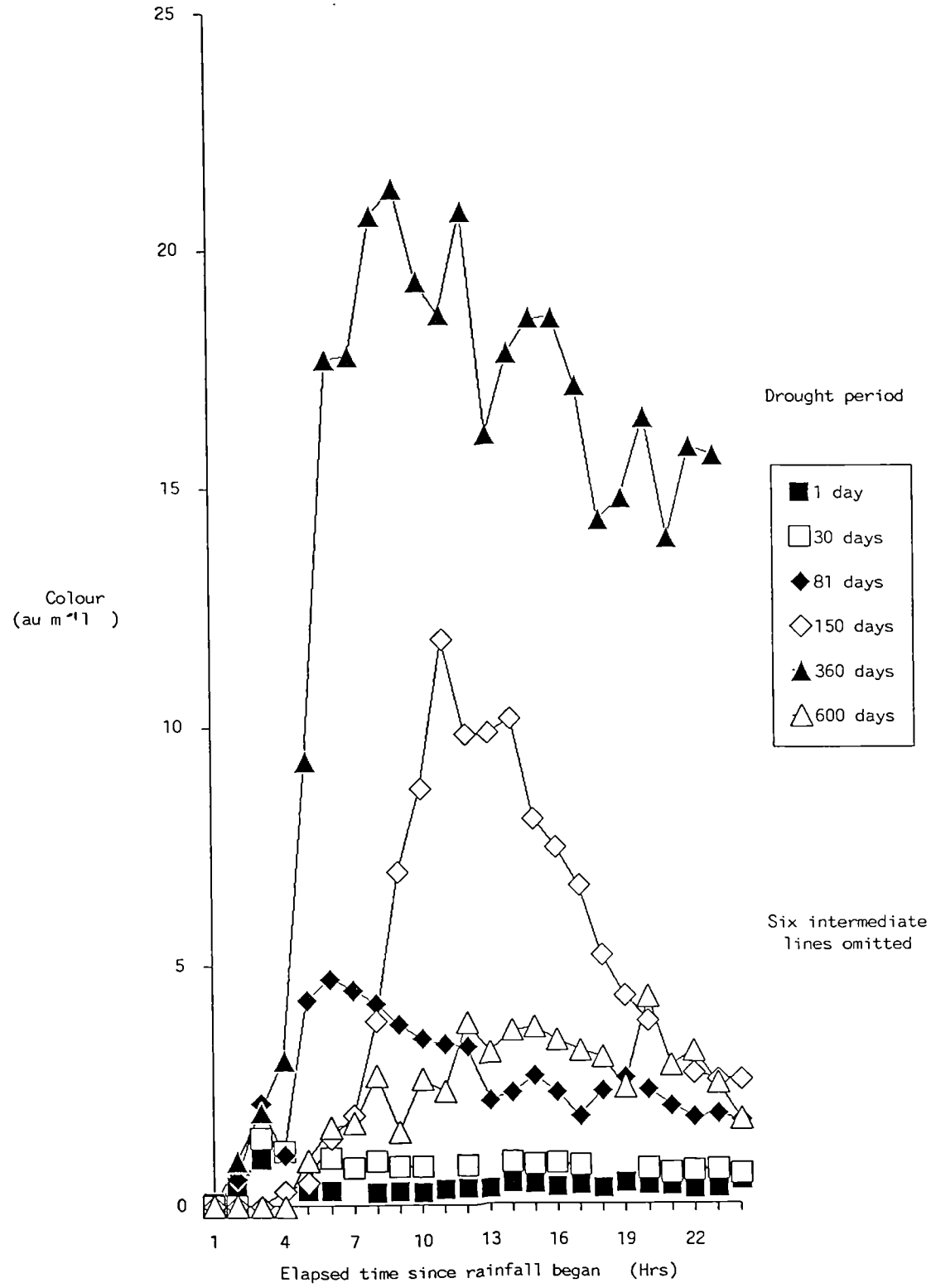
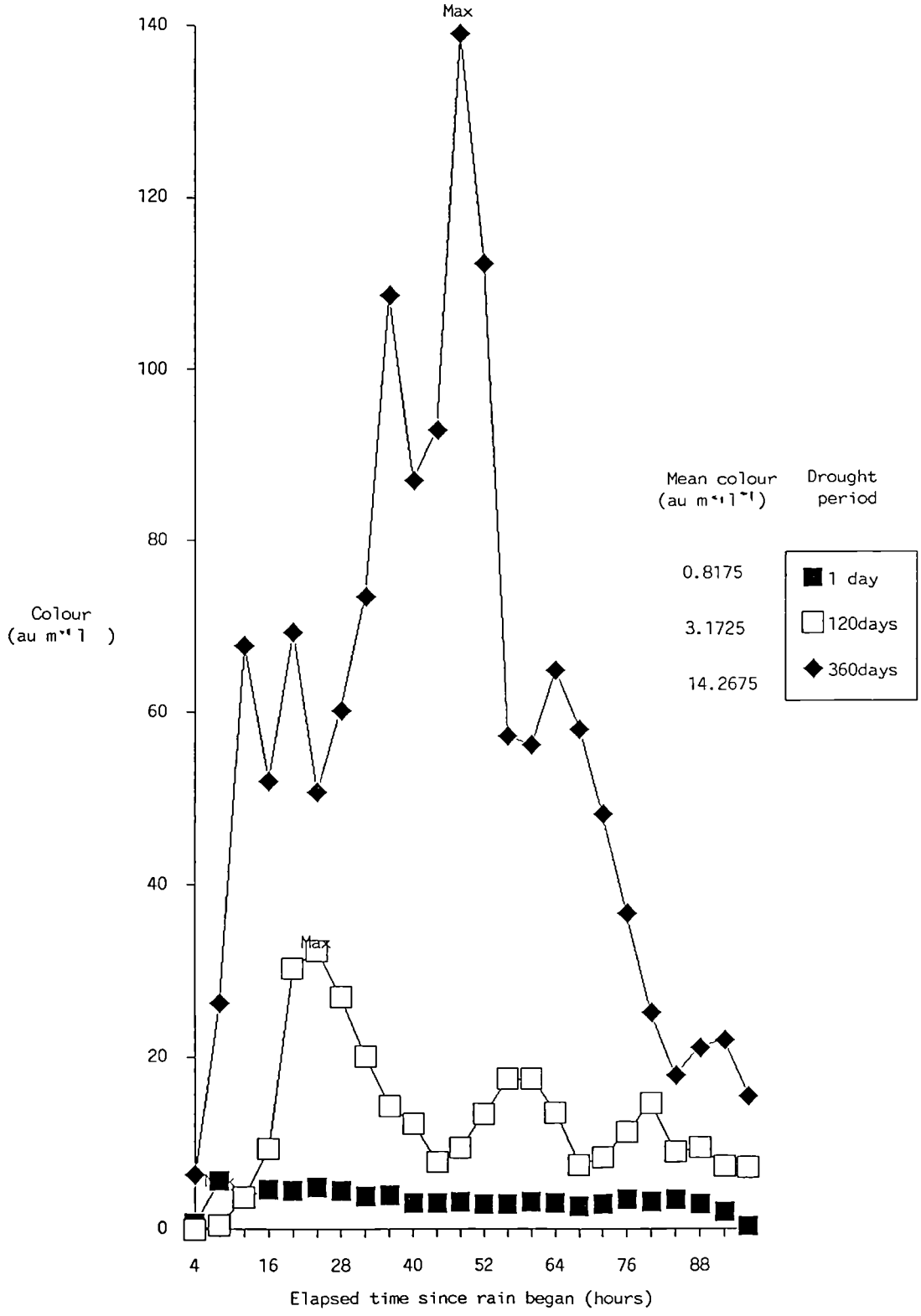


Figure 5.12 Pattern of colour release from droughted peats during rainfall simulation



increases thus taking the time of peak response beyond 24 hours. After omitting these two observations regression analysis of colour on drought period gives the relationship:-

$$TCO_{24} = 0.576\ S + 1.3 \qquad (2)$$

Where S is drought period in days. This relationship is highly significant ($r = 0.713$, $N = 19$, $P < 0.001$) and demonstrates that the store of water soluble colour in the peat cores increases as a function of drought duration. The Pearson correlation coefficients between TCO_{24} and moisture content at each depth interval were determined and are presented in table 5.7.

Table 5.7 Pearson Correlation coefficient between total colour output (TCO_{24}) and peat moisture content.

depth Interval (cm)	R	N	Prob
0 - 3	0.916	18	< 0.001
3 - 9	0.733	18	< 0.001
9 - 15	0.588	18	< 0.01
15 - 23	0.459	18	< 0.01

Near surface drying has the strongest single influence on the production of a soluble colour store. Peat moisture content determinations at each depth interval indicate the role of the surface and near surface peat in acting as a 'protective crust', preventing anything more than light dewatering below 3 cm. At the surface (0-3 cm)

all peats sampled had lost at least 25 % moisture after 50 days drying. However, at 3-9 cm and 9-15 cm 25 % moisture loss is attained only after 360 and 600 days drought respectively. Below 15 cm peat moisture content remains above 80% even after 600 days drought. The protective crust, while preventing drying beneath it, is itself subject to great aerobic decomposition and oxidation processes. This is thought to result in enhanced organic matter breakdown and increased availability of water soluble, colour forming organics.

Products of organic matter breakdown are only translated into colour on contact with water. For each peat sample the per cent moisture before and after rainfall simulation was determined at each depth interval. The difference between these observations determines the degree to which the peat has rewet (δM). The correlation coefficients between TCO_{24} and rewetting (δM) at each depth interval were determined. These are presented in table 5.8.

Table 5.8 Pearson correlation coefficient between total colour output (TCO_{24}) and rewetting (δM) at the specified depth intervals.

depth Interval (cm)	R	N	Prob
0 - 3	0.957	18	< 0.001
3 - 9	0.772	18	< 0.001
9 - 15	0.340	18	> 0.01
15 - 23	0.410	18	> 0.01

These results indicate that rewetting of the surface peat layers are strongly related to and may be responsible for the greatest proportion of discoloration. At depth there is little drying due to the structure of the peat and the protective surface crust, resulting in only a small increase in the store of soluble decomposition products. Therefore, rewetting in these lower peat layers cannot account for water discoloration. The near surface peat has been subject to more extensive drying producing a larger colour store. When this peat rewets the soluble organic store is mobilised and removed as coloured water.

Stepwise regression of TCO_{24} with moisture content before and after rainfall simulation, and moisture change for each depth interval was able to account for 92.43 % of the variation in TCO_{24}. However, the change in moisture content of the near surface peat (0-3 cm interval) was able to account for 91.58% of the variation alone (figure 5.13), therefore:

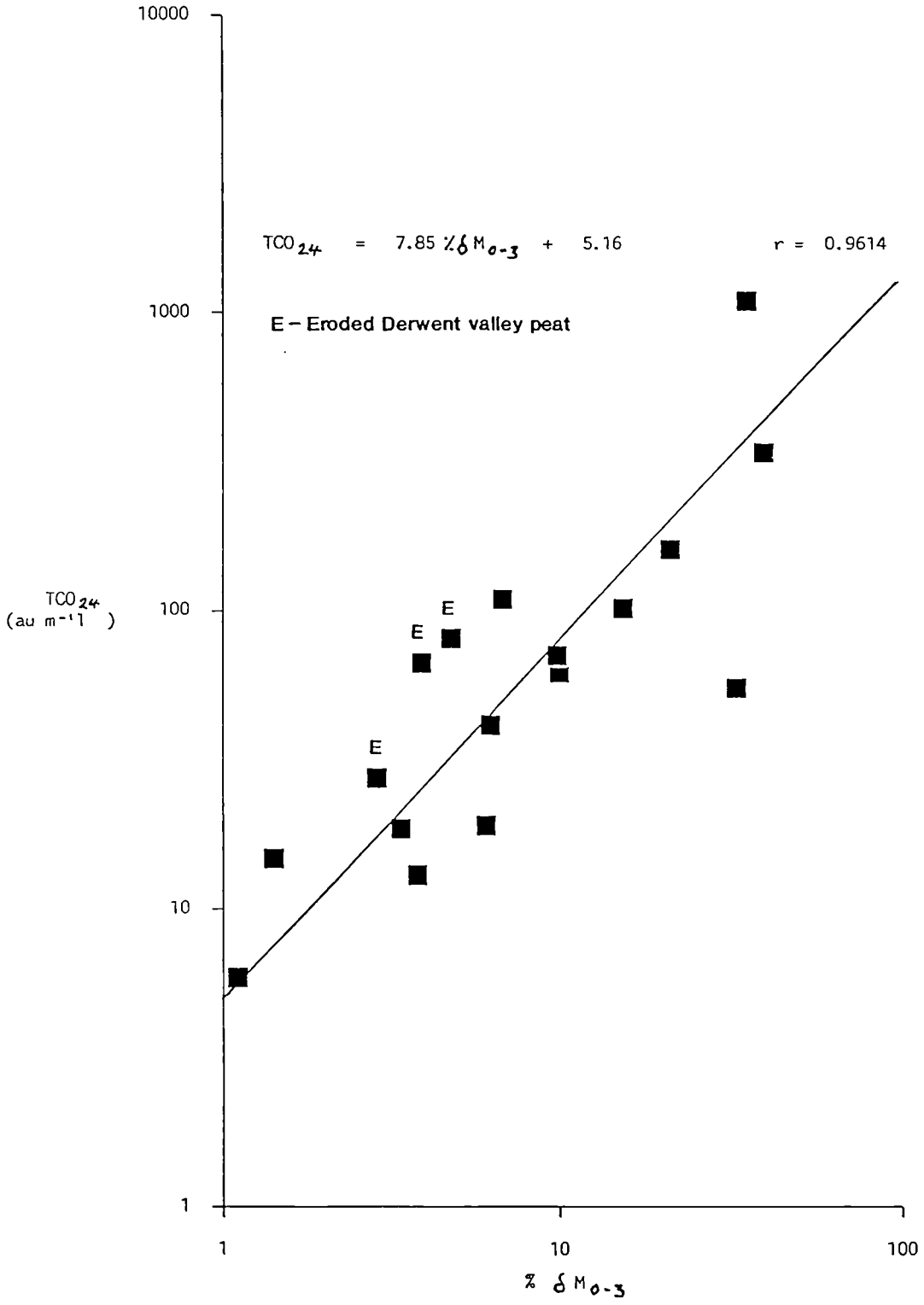
$$TCO_{24} = 7.85\ \delta M_{0-3} + 5.16 \qquad (3)$$

Where δM_{0-3} is the change in moisture content of the 0-3 cm interval on rewetting. The next most significant variable, δM_{3-9} adds less than 1 % to the total explained colour variance.

5.4.3 Discussion

The natural discoloration of water results from the action of two basic processes. These are firstly, the accumulation

Figure 5.13 Relationship between TCO_{24} and rewetting of surface peat during rainfall simulation



of water soluble organic decomposition products, and secondly, their subsequent removal by water. These may be considered as processes of colour production and removal.

(a) Colour production

Previous results indicate that water is coloured by water soluble organic decomposition products. Decomposition occurs as a result of oxidation and the action of soil microbes. Models of soil aggregates (Emerson, 1959; Greenwood, 1968) suggest that decomposition rates are greatest on the internal walls of soil pore spaces, and depend on whether they are air or water filled. In Winter Hill Association peat the aerobic decomposition rate was found to be approximately three times the anaerobic rate (chapter six). Thus the quantity of decomposition products, and therefore colour production, is thought to be largely dependent on the total peat pore space surface area exposed to air. Table 5.9 gives the hypothetical distribution of soil pore frequencies as a function of pore diameter (after Loxham and Burghardt, 1986).

The rapid moisture loss experienced by saturated peats in the initial stages of drying is a result of dewatering from the large diameter pores with low suction pressure. Dewatering of these pore spaces results in the exposure of peat to aerobic bacteria and oxidation processes, the subsequent breakdown of organic matter, and thus production of a colour store. Organic matter breakdown continues if further pore space surface areas are exposed.

This requires either the physical disturbance of the peat structure or further drying to dewater pores with progressively higher suction pressures. Physical disturbance is most commonly a result of changes in soil moisture status, and is likely to result in the removal of those water soluble organics already produced. Thus it is continued peat drying that is likely to be the most significant factor in the growth of the colour store.

Table 5.9 Theoretical peat pore size-frequency distribution

pores per cm^3	Pore diameter (u)	Pore volume (m^3)	Pore internal surface area (m^2)
10^2	300	7×10^{-9}	2.8×10^{-4}
10^4	30	7×10^{-10}	2.8×10^{-4}
10^6	3	7×10^{-11}	2.8×10^{-4}
10^8	0.3	7×10^{-12}	2.8×10^{-4}
10^{10}	0.03	7×10^{-13}	2.8×10^{-4}

Due to compression by overlying peat, sub-surface peat is deficient in larger pore spaces. However, surface peats have a relative abundance of these larger pore spaces due to root growth, movement of soil fauna and absence of overburden. This produces a skewed pore frequency-diameter distribution. Given this skewed distribution, with large pores dominant in the surface peat, and small pores dominant below, drying results in a rapid moisture loss at the surface, with a relatively small exposure of

internal pore surface areas. At depth, dewatering could produce an increase in exposed internal surface areas over a range of up to four orders of magnitude (table 5.10). Thus at depth, a uniform volume of peat may have up to 1 x 10^4 times the total internal surface area of near surface peat.

A prolonged drought will thus draw out water from pores with smaller volumes, higher suction pressures, and a much greater total internal surface area. This will result in a considerable increase in organic matter breakdown and produce a larger colour store. In the near surface peats the rate of colour accumulation increases when the drought period exceeds 120 days. This may be the point at which a particular pore size first becomes dewatered allowing decomposition processes to add to the colour store.

Table 5.10 Theoretical pore surface area-diameter distribution

Pore diameter (μ)	Internal surface area (m^2)	Pore volume (m^3)	Number pores per 300μ pore	Relative surface area(m^2)
300	2.8×10^{-7}	7×10^{-12}	1	1
30	2.8×10^{-9}	7×10^{-15}	1×10^3	10
3	2.8×10^{-11}	7×10^{-18}	1×10^6	1×10^2
0.3	2.8×10^{-13}	7×10^{-21}	1×10^9	1×10^3
0.03	2.8×10^{-15}	7×10^{-24}	1×10^{12}	1×10^4

(b) Colour removal

Decomposition products are removed by the movement of water. Some of these products are water soluble, and will discolour water. The extent of discoloration is determined by the degree to which water can access pore spaces, rewetting the peat, and removing the colour store. Under rainfall simulation the degree of discoloration of peat core throughflow was directly proportional to the extent of near surface peat rewetting. The near surface peats experience the greatest drying and so have the largest colour store to be released on rewetting.

Severely dried peats (≥ 25 % moisture loss) appear particularly resistant to rewetting. These peats produce the most intense colour flushes, with the greatest colour flux following rewetting (figure 5.14). Resistance to rewetting is probably due to macro-pore collapse following drying, and to high suction-pressures found in micro pores. In addition, drying causes humic macromolecules to shrink, binding organic fractions responsible for colour (Hayes, 1987). On initial wetting these peats will shed water, preventing the removal of organic matter. However, continued wetting will eventually lead to access of water to all pore spaces, resulting in saturation and the removal of the colour store. For changes of up to 50 % in peat moisture content, permeability can range over five orders of magnitude (Loxham and Burghardt, 1986). During rainfall simulation it took several days continual rainfall until

5.14a Moisture loss ($\%M_{0-3}$) in surface peat following induced drought

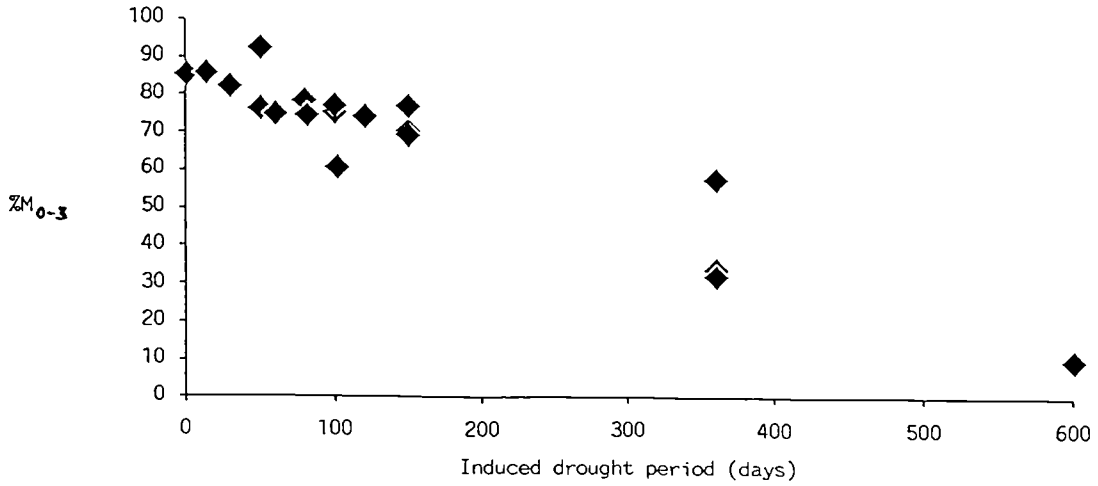
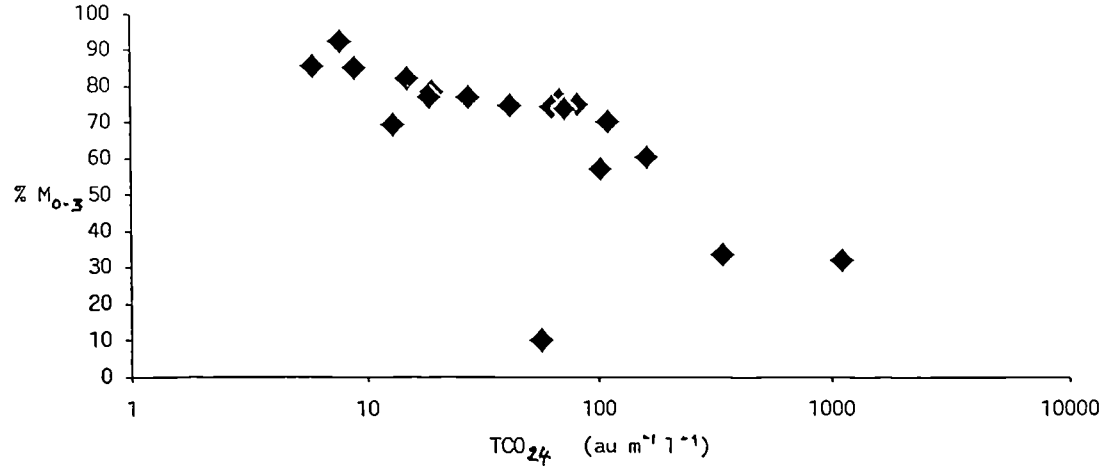


Figure 5.14b Relationship between TCO_{24} and rewetting of surface peat during rainfall simulation



peak colour output was reached (figure 5.12). Peat samples subject to prolonged drought, particularly with moisture loss in excess of 30 %, have the longest delay before peak colour output, and have the greatest colour flux.

5.4.4 Implications for moorland management

Any action that causes severe drying at the peat surface (≥35% water loss) will greatly increase the store of decomposition products that can discolour water. The pattern of colour release from the eroded Derwent valley cores was consistent with their drying and rewetting (figure 5.13). These cores are thus not dissimilar to the other peats examined. Thus peat erosion is not thought to increase colour per se, but results in increased colour due to enhanced surface drying. Eroded peats dry more readily due to a lower albedo, and an absence of plant roots transporting water to the surface.

Similarly moorland drainage ditches expose large surfaces of bare peat contributing to severe drying and colour release on rewetting. Heavy drying of bare peat also results in vertical cracking, greatly increasing the total area on which drying processes act. Moorland burning will also act to increase the colour store by lowering infiltration capacities and enhancing drying of sub-surface peat. These actions may dry near surface peat to a far greater extent than any natural drought, producing water of extreme colour when complete rewetting eventually takes place. It has previously been noted that the colour

of standing water in one heavily ditched sub-catchment of the Upper Nidd valley was observed to be in excess of 1000 au m^{-1}. In addition, eroded and burnt peats have darker surfaces, lower albedos and therefore greater energy absorption and higher temperatures which may act to encourage microbiological decomposition.

Severe peat drying, whether as a result of erosion, ditching, burning, or simply through prolonged natural drought, greatly increases the accumulation of decomposition products. The capacity of these peats to rewet quickly is much reduced prolonging the available time for decomposition, so that when saturation is achieved runoff will carry a very high load of water discolouring organic solutes.

5.5 The effect of temperature on colour release during rainfall simulation

The effect of soil temperature on colour production in peat was examined using the rainfall simulation technique. All samples were of equal size, weight and moisture content on collection. They were then stored at 8°C, 25°C, 37°C and 44°C, wrapped in polythene in humid conditions, for seventeen days. Peat moisture contents between samples varied by ≤ 5% following storage. A large needle bed rainfall simulator was used enabled all samples to be flushed simultaneously. A rainfall rate equivalent to 155 mm d^{-1} was employed to wash out the colour store. Total colour output from these peats were:

Peat storage temperature (°C)	8	25	37	44
Total colour output (au $m^{-1}l^{-1}$)	3.9	18.1	33.2	11.6

Total colour output increases with temperature up to 37°C, after which, at 44°C it falls to below the 25°C value. Colour output reaches a maximum at 37°C, which is coincident with the optimum temperature for coliform culture. This pattern of colour output may indicate temperature dependent microbiological activity, although the degree of replication does not allow any statistical significance to be attached to these results.

5.6 The effect of methods of peat drying on colour generation

Rainfall simulation has demonstrated that water discoloration is closely associated with soil moisture deficit, while earlier investigations have indicated that soil temperature may also be significant in discolouration, probably through the action of soil micro-organisms. Therefore, the effect of low and high temperature peat drying on discolouration was assessed.

Winter Hill peat collected from Scar House pasture, Upper Nidd (SE 068 762) was progressively dried according to two treatments. The first treatment consisted of oven drying peat at 120°C for up to six hours, producing moisture contents varying from 10-85 %. The second, low temperature treatment, consisted of prolonged 'natural' drying. Peat samples were taken from 10 kg peat cores,

stored outdoors for periods up to twelve months, but with all precipitation excluded. These peat samples dried to moisture contents ranging from 20-95% (w/w). Peat samples ($8cm^3$) were then placed into 250 ml of distilled water and extract colour was determined after shaking the mixture at 400rpm for 16 hours. The results are illustrated in figure 5.15.

A clear difference in extract colour exists between the two treatments. The pattern of colour in the naturally dried peats is consistent with earlier observations, with colour increasing as a result of peat drying. A very rapid colour rise from 95-75 % moisture is evident, followed by a less rapid increase with still drier peat. Oven drying peat results in a steady decline in extract colour. This difference is not significant for the whole data set due to the high variability in the low temperature treatment group. However, if samples with minimal drying ($\geq$ 80 % moisture) are excluded from the analysis it is evident that there is no significant difference in the degree of drying experienced ($t=0.943$, $df=10$), but that the low temperature treatment produces significantly more colour ($t=2.231$, $df=10$, $P< 0.05$).

These results are interpreted in terms of peat rewetting and colour production. Firstly, severe drying may produce hydrophobic cavities within the peat, preventing easy penetration of water to pick up solutes. This may explain why a colour decline is seen in oven dried peats. However, the 'naturally' dried peats were dewatered to the same

Figure 5.15 Effect of method of peat drying on extract colour

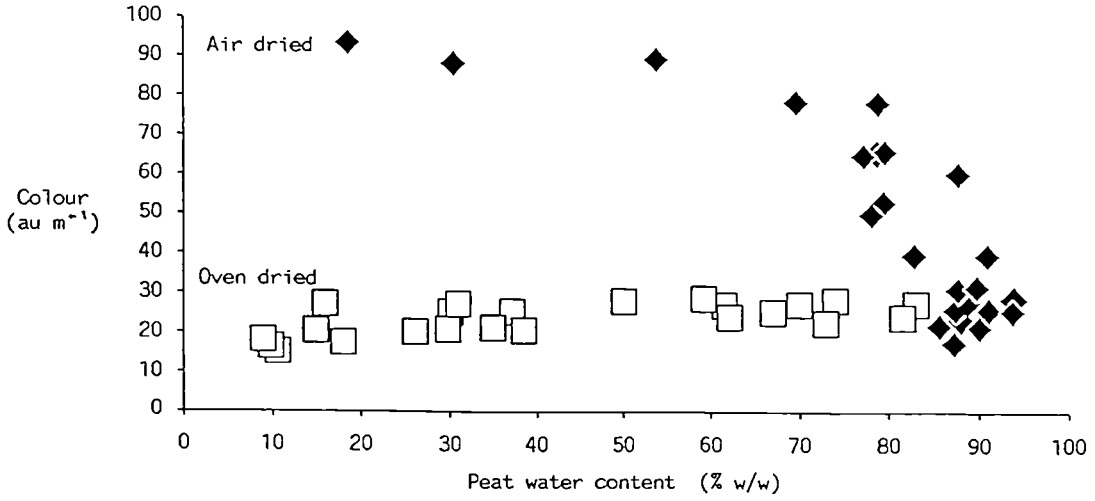
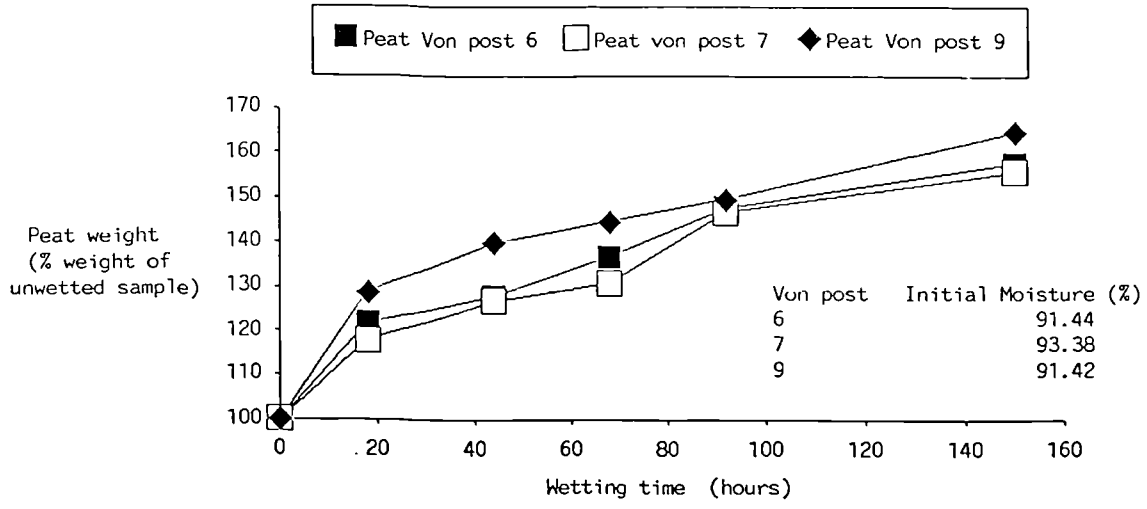


Figure 5.16 Peat wetting rate with no prior drying



extent and no colour decline was observed. This suggests that a second, more important mechanism operates. The major differences between the drying methods involved time and temperature. Long storage times allows the maximum growth and activity of microbiological populations, while high temperatures may reduce or eliminate them. Such populations may be crucial to the decomposition of insoluble organic material, such as lignins, cellulose and carbohydrates, into water soluble fractions such as humic and fulvic acids, thought to be responsible for colouring water.

5.7 Peat rewetting potential

Results from previous investigations indicate that colour release from peat is directly proportional to the increase in moisture content following drying and rewetting. However, there is a departure from linearity of this relationship when peat experiences severe moisture loss. Peat subject to a 'natural' drought in excess of 120 days lost ≥ 25 % moisture and produced very high colours during rainfall simulation. However, these peats produced less colour than expected, unless subject to many days rainfall. Similarly, the intensity of colour extracted from naturally dried peat increased rapidly when dried by up to 25%, but the rate of increase was much less with moisture loss in excess of 25 %. These results suggest that the extent of soil moisture loss effects the timing and intensity of coloured flows through the ability of a peat to rewet.

A principal feature of humic materials is their ability to absorb and retain large quantities of water, peat typically comprising 80-95 % water (w/w). However, when dried, much of the capacity of a peat to absorb water, to rewet, can be lost, particularly under high temperatures. Schallinger (1972) reported a 65 % loss of water retention by peat after air drying and 75 % after oven drying, while Vendure (1976) reported that the rewetting capacity of peat can be impaired under field conditions.

No definitive theory for a reduction in rewetting potential (RWP) has been tested and found valid. Reduced rewettability may be due to mechanical or chemical changes taking place within the peat, or a combination of the two. With small reductions in water content, reduced rewettability is most likely due to macro pore collapse, while micro pores and fine capillaries are not likely to be affected until there is a significantly higher reduction in water content. Chemical changes associated with impairment of rewetting are potentially numerous, and may relate to the concentration of hydrophobic groups such as methoxyls, and strongly hydrophillic groups such as hydroxls, both of which are related to plant decomposition. Mechanical effects, such as pore collapse, should be prevalent near the surface of a peat profile, where considerable water table fluctuation may be experienced. Chemical effects of dewatering may be more significant deeper down the profile, where greater degradation has taken place. Thus RWP may be a function of depth and

decomposition. Rewetting potential, as a function of moisture loss was determined for Winter Hill peat.

5.7.1 Methodology

There are two basic steps involved in determining a peats RWP. The peat must first be brought to a standard moisture content, after which it is dried and subsequently rewetted. The standard moisture content is experimentally defined by completely immersing peat in water for twelve hours, followed by a two hour free drainage period. The peat is then said to be saturated. Peats are rewet by again immersing in water. The weight of the sample following drying and rewetting, expressed as a percentage of the saturated peat weight is the rewetting potential.

Preliminary experiments using the methods of Feustel and Byers (1930) and Brown and Farnham (1978) were unsatisfactory. In their methods drainage after saturation takes place through mesh screens, but it was found that with small mesh sizes Scar House peats drained very slowly, while peat was lost in solution if a larger mesh was used. In the following experiments peats were saturated, drained, dried and rewetted in calico bags. The change in weight of these bags during the experiment is insignificant as they are saturated before use, and dry to constant weight within 15 minutes during the drying process. Peat samples were oven dried at 105°C for up to six hours. Water losses up to 90% were achieved.

Three peats were used, with varying degrees of decomposition. They were collected from the surface of Scar House pasture, where peat was highly fibrous, from a depth of 65 cm where greater decomposition was apparent, and from a hagg where the peat was highly amorphous. The Von post decomposition values were 6,7 and 9 respectively. The Von post scale (Von post and Gränlund, 1926) decribes peat decomposition based on observations of recognisable plant remains, and the quantity of peat and turbidity of water extruded on squeezing. Avery (1980) details a commonly used, modified version of the scale.

5.7.2 Results

As a control experiment, the change in peat weight with prolonged wetting and no prior drying was determined (figure 5.16). All peats rapidly absorb water, and, even after 150 hours immersion constant weight has not been achieved. The most highly decomposed peat (Von post = 9), consistently absorbed more water than the less well decomposed peats ($t=2.842$, $df=5$, $P < 0.05$).

The ability of peat to rewet after drying is shown in figure 5.17. With water loss ≤ 10 % peat has a high RWP, regaining all, and in some cases more, of the water lost during oven drying (RWP can exceed 100 % as the standard saturation time is 12 hours, whereas the rewetting periods here are 18 and 90 hours). With significant water loss RWP is generally well below 100%, even after 90 hours rewetting, indicating that the ability of these heavily

Figure 5.17 Rewetting potentials of peat (Von post 6)

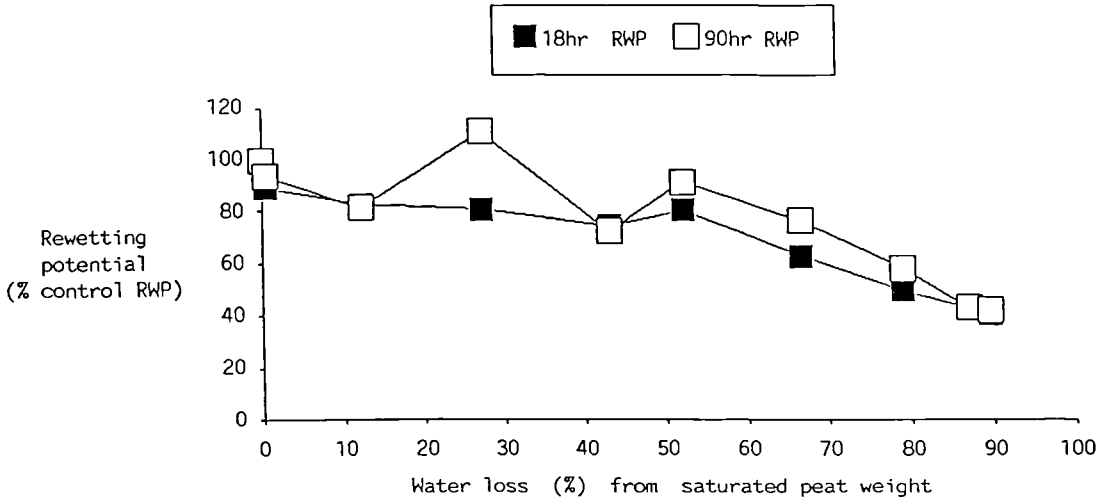


Figure 5.17 (cont) Rewetting potential of peat (Von post 7)

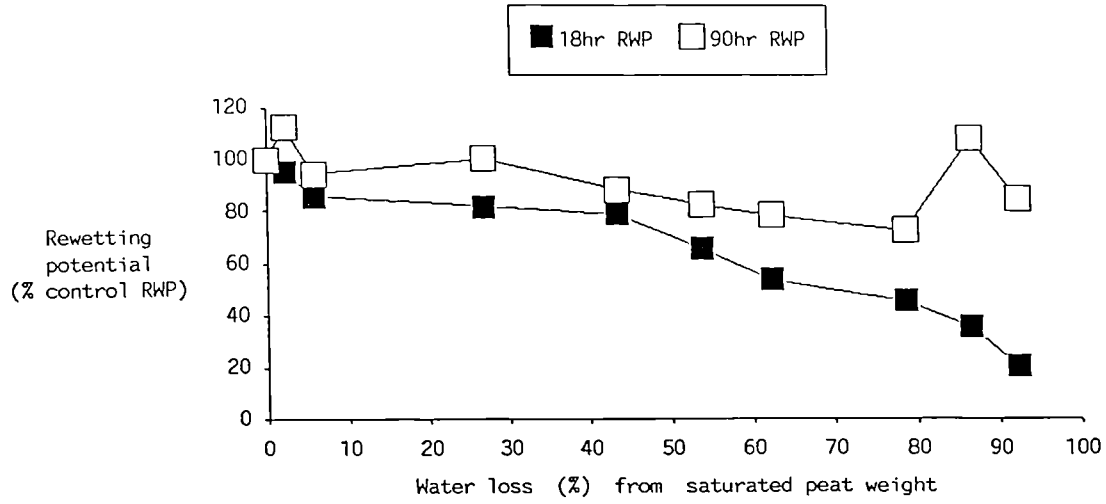


Figure 5.17(cont) Rewetting potential of peat (Von Post 9)

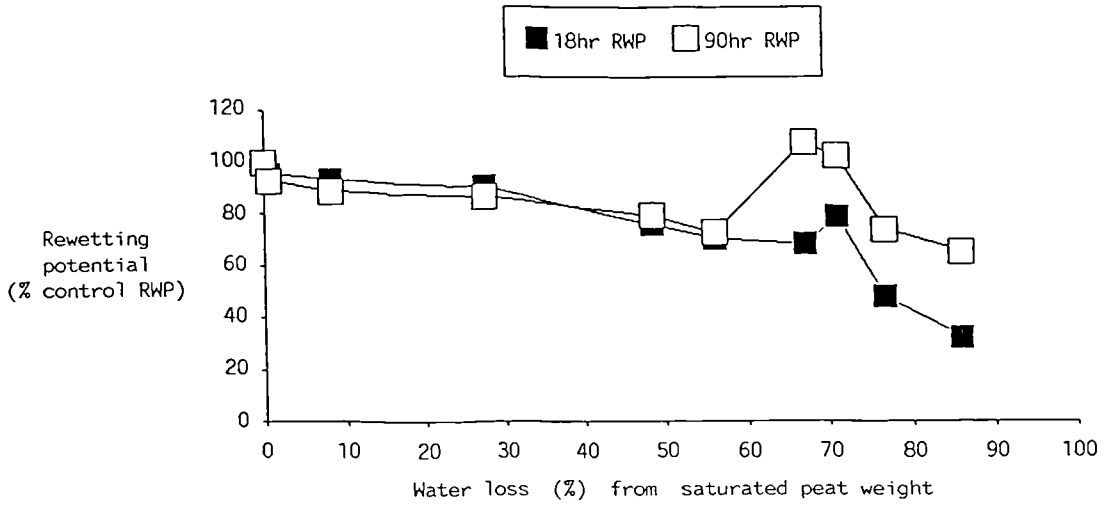


Figure 5.18 Change in ten day rewetting potential (Von post 6)

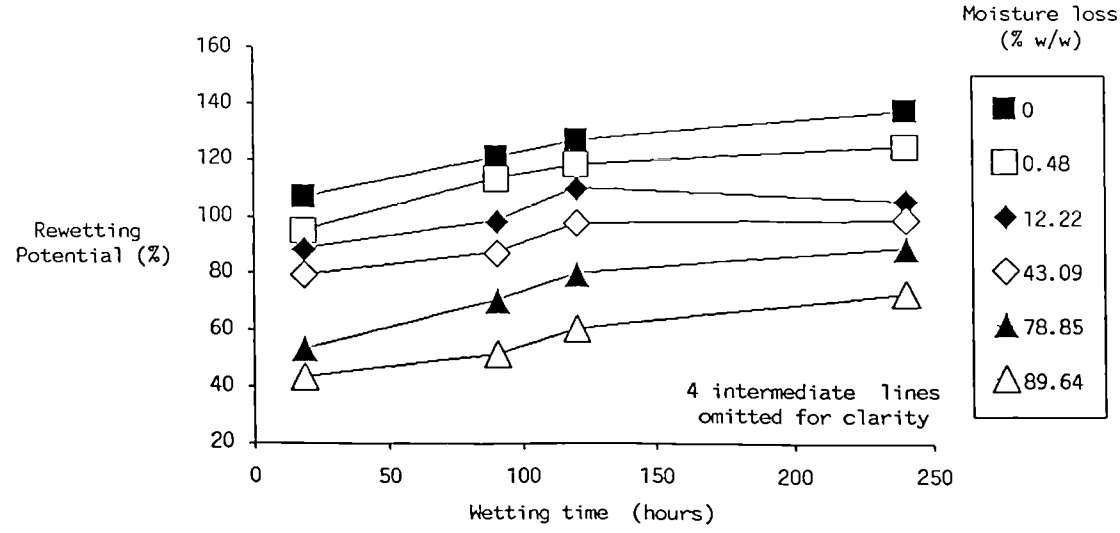


Figure 5.18(cont) Change in ten day rewetting potential (Von post 7)

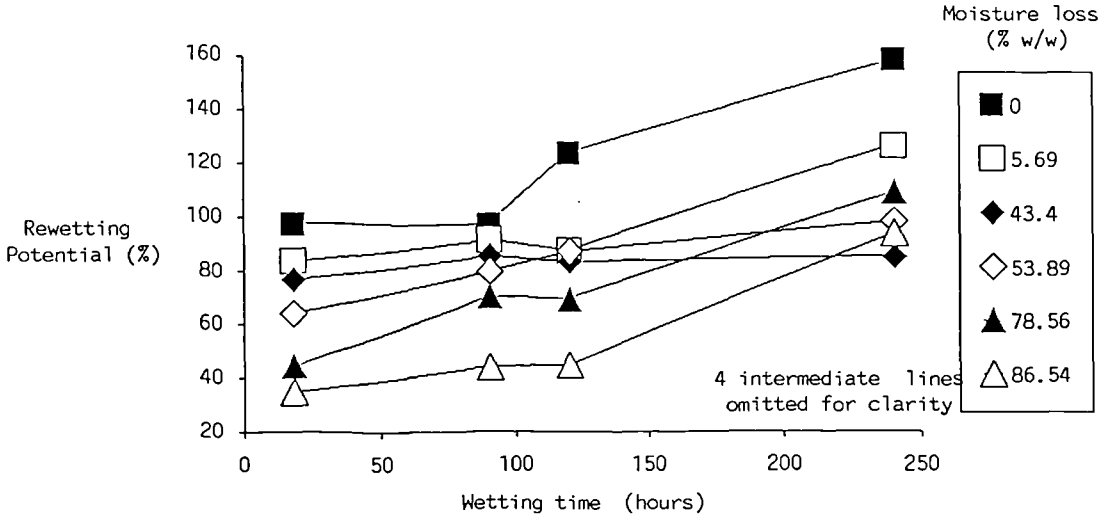
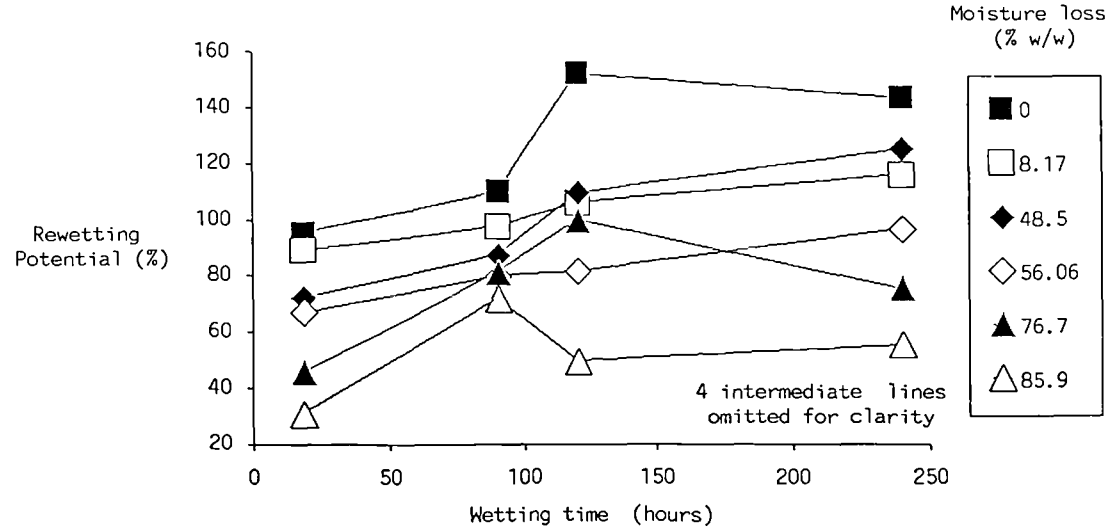


Figure 5.18(cont) Change in ten day rewetting potential (Von post 9)



dried peats to absorb water has been greatly impaired. With all peat types the rewetting potential was greater after 90 hours rewetting ($t=5.88$, $df=29$, $P=0.001$), illustrating the recovery of the peat towards saturation. There was no significant difference in moisture loss between the three peat types, and at 18 hours no significant difference in their RWP's. However, after 90 hours it is apparent that these peats have rewet at different rates, with the least decomposed peat rewetting very much slower than the others, particularly at high moisture loss (Von Post 6-9, $t=1.803$, $df=9$, $P<0.05$; Von post 6-7, $t=4.638$, $df=9$, $P<0.001$). This suggests that rewetting of poorly decomposed peats, such as the surface peat studied here, is adversely affected by macro-pore collapse. Macro-pores are thought to be more abundant in poorly decomposed peats.

A further test was conducted with rewetting times up to 240 hours. RWP's were determined after destructive sampling. Results are presented in figure 5.18. Once again RWP's increase with rewetting time, and depend on the degree to which the peat was dried. Heavily dried peats are very slow to rewet, some not regaining their initial wet weight, even after 240 hours complete submergence. Moisture loss was negatively correlated with 18, 90, 120 and 240 hour RWP's ($P<0.001$). These observations were used to estimate the critical moisture loss of the peats used. The critical moisture loss is defined as the degree of drying that prevents a peat from regaining its saturated state after 240 hours immersion. For all peats the 240 hour RWP was

regressed against sample moisture content. Moisture loss approximated to the normal distribution (kurtosis = -1.50, Skewness = -0.13), but the fit could not be improved by any simple transformation. The resultant regression equation was:

$ML_C = -0.84017\ (CRWP_{240}) + 135.67 \quad r^2=0.5373,\ P < 0.0001$

where ML_C = critical moisture loss

$CRWP_{240}$ = RWP of non-dried peat

To obtain a value for ML_C the 240 hour RWP for the control peat value must be entered into the equation. This value is not 100 % as the rewetting period exceeds the initial saturation period, twelve hours, after which the peat continues to absorb water, as discussed above. Control peats were those which dried by ≤ 5 %. The mean RWP_{240} for control peats was 134.50. Substituting this value into the above equation gives a value for ML_C of 22.67%. This value is similar to those reported in the literature and significantly, is in close agreement with the moisture loss value (25 %) where moisture loss and colour production depart from linearity (figures 5.14a, 5.14b). The data was sub-divided to allow ML_C determinations to be made for each peat type. Results are presented in table 5.11.

Table 5.11. Critical moisture loss (ML_C) by peat type.

Von post	r^2	P ANOVA	m	c	ML_C (%)
6	0.4101	0.0461	-0.90171	147.98	29.13
7	0.5275	0.0174	-0.73595	124.62	20.04
9	0.79525	0.0005	-1.03717	150.31	15.97

Peat is able to absorb water quickest, and rewet following drying quickest when it is well decomposed. This may be due to differences in pore-size distribution in peats. Smaller pores, more abundant in well decomposed peats, have high suction pressures absorbing water quickly. However, results indicate that well decomposed peats have a low critical moisture loss value. The ML_c value may denote the point at which micro-pores begin to lose water, collapse, and are unable to rewet. Less well decomposed peats are effectively buffered from severe drying by their relative abundance of macro-pores.

The implication for colour release is that peats that dry beyond their critical moisture loss become hydrophobic. Hydrophobic peats are then subject to maximum decomposition, and therefore the production of very large in situ colour stores. Peats that readily rewet may experience significant decomposition. However, they do not contribute to very high water colours as they are continually being flushed & do not have the opportunity to produce large colour stores. Aerobic colour production may continue for some time in hydrophobic peats even when below the water table. The colour store will be flushed from the peat when it does eventually rewet producing an intense colour flush. Rewetting is likely to be well in excess of ten days complete saturation, contributing to a lag time between rainfall and runoff colour. The critical moisture losses determined here are relatively low, and are likely to be exceeded during summer drought, following moorland

burning, and where peat is not protected from drying by vegetation, such as on ditch faces and in areas of erosion.

5.8 Comparison of water colour and pH from surface and deep peats following naturally induced drying

The influence of peat depth on colour production was studied. Winter hill peat samples were collected from Scar House pasture at depths of 0-5 cm (D_0), 95-105 cm (D_1) and 195-205 cm (D_2). Samples were evenly spread to a depth of 2 cm and allowed to air dry at 18°C for up to 31 days. Throughout the drying period 10 ±0.01 g sub-samples were taken for determinations of moisture content, extractable colour and peat pH. Moisture determination was made by drying to constant weight at 105°C, extractable colour by shaking peat samples in distilled water (1:10) at 220 rpm for 16 hours, and peat pH after shaking peat in 0.01 M $CaCl_2$ (1:5) for 16 hours at 220 rpm. The response of extract colour and peat pH to soil moisture loss is illustrated in figures 5.19 and 5.20.

Lumping data from all three depth categories demonstrates that extract colour is correlated with soil moisture ($r=-0.4682$, $N=84$, $P<0.001$) and peat pH ($r=-0.2841$, $N=84$, $P<0.01$). Peat pH is also correlated with soil moisture ($r=0.6236$, $N=84$, $P<0.001$). This is consistent with earlier observations, and demonstrates that peat drying promotes decomposition. Decomposition products, including organic acids increase soil acidity, and when soluble in water are manifest as colour.

Figure 5.19 Change in extract colour from surface and deep peats following induced drying

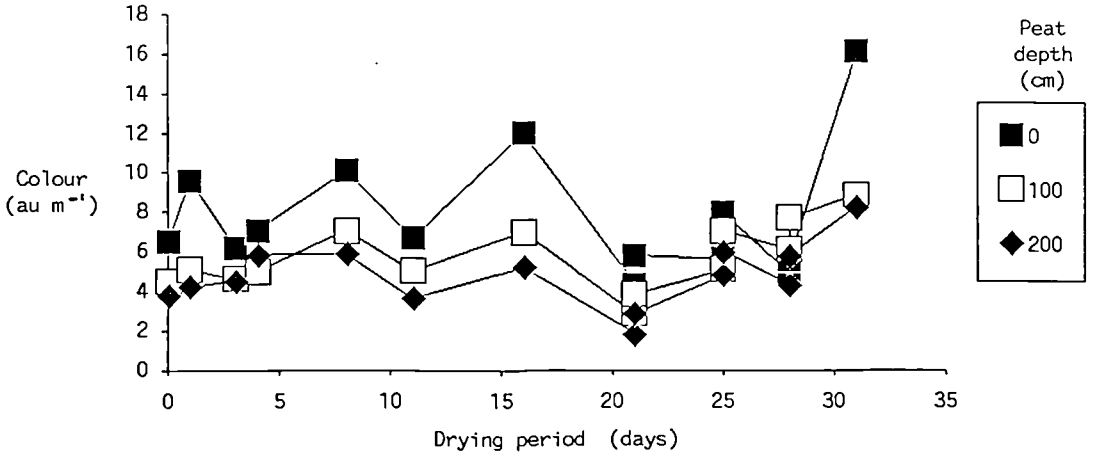


Figure 5.20 Change in peat pH of surface and deep peats following induced drying

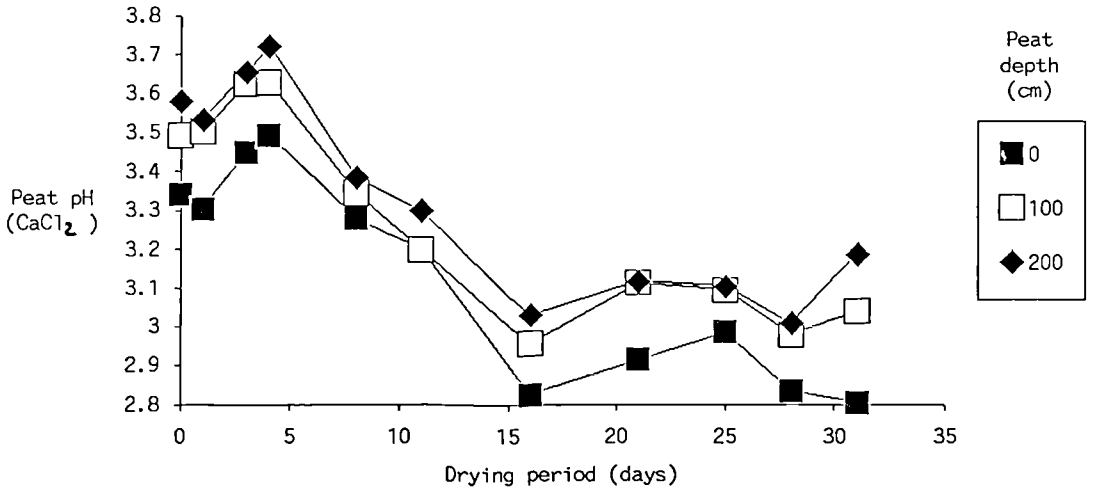


Table 5.12 Differential colour-pH-moisture response of deep and surface peats to uniform drying intensity.

Peat depth (cm)		0-5	95-105	195-205
Moisture (%)	Mean	78.01	82.63	86.55
	Min	60.08	55.06	70.76
	Max	89.30	90.91	93.85
Colour (au m^{-1})	Mean	7.75	5.70	4.79
	Min	4.10	2.60	1.60
	Max	20.60	10.30	9.00
Peat pH ($CaCl_2$)	Mean	3.08	3.22	3.29
	Min	2.79	2.95	3.00
	Max	3.52	3.67	3.73

Peats collected from different depths display a differential response to drying (table 5.12). Extract colour decreases with increasing peat depth ($D_0 > D_1$, $t=2.32$, $N=28$, $P<0.05$; $D_1 > D_2$, $t=4.59$, $N=28$, $P<0.001$). Similarly peat pH increases with depth ($D_0 < D_1$, $t=6.66$, $N=28$, $P<0.001$; $D_1 < D_2$, $t\geq10$, $N=28$, $P<0.001$).

These results are interpreted in the light of soil moisture loss. Although peats from the three depth categories were all subject to equivalent drying intensity, they did not dry at the same rate. Following uniform drying conditions soil moisture increases with peat depth ($D_0 < D_1$, $t=3.30$, $N=28$, $P<0.01$; $D_1 < D_2$, $t=1.78$, $N=28$, $P<0.05$). This indicates that surface peats are least resistant to drying

influences. They are therefore subject to greatest decomposition, producing most colour and acidity. This is consistent with the rewetting potential of peats discussed above. Surface peats dry more readily as water is loosely held in macropores. Deeper peats are richer in micro pores with higher suction pressures and are therefore more resistant to water loss. Few samples dried to a point beyond their estimated critical water loss, suggesting that most colour production has taken place in macro-pores.

5.9 The impact of soil and water pH on drainage water colour.

In chapter two it was demonstrated that colour is pH dependent. Raising the pH of a humic water increases its colour as more organic matter becomes soluble. It has also been demonstrated that more colour is released from peat in particular pH ranges, and a general increase in colour release is found with increased pH. This implies that the pH of a peat, and the pH of the water flushing a peat, has a significant influence on the solubility of dissolved organic matter, and therefore the ability of the peat to colour water. In this section, the effect of peat drying on runoff pH and of rainfall pH on peat pH and colour solubilisation is studied.

5.9.1 The effect of drought on drainage water pH

A previous study investigated the impact of induced drought on colour released from Winter Hill peat during rainfall

simulation (section 5.4.1). In addition to colour measurements, throughflow pH was measured, using a low conductivity probe. Measurements were made hourly, over a 24 hr period, for peats droughted from 0 to 360 days. Rainfall pH was maintained at 5.0 ±0.2. Results are illustrated in figure 5.21.

The pattern displayed by throughflow pH is broadly similar to that of colour. An initial acidic flush is followed by a slow, but steady increase in pH throughout the simulation period. Mean throughflow pH and colour (TCO_{24}) are correlated ($r=-0.5460$, $N=15$, $P<0.05$). Peat subject to prolonged drought has the most acidic throughflow, and the slowest recovery rates. Mean pH decreases with drying in an approximation to an exponential decay (figure 5.22). With no drying mean throughflow pH is 4.5. This falls by over 1.5 units after 50 days drought, and nearly 2 units after 150 days. If peats that have not begun to rewet are excluded from the analysis then drought duration and pH are correlated ($r=-0.8051$, $N=13$, $P < 0.001$).

These results demonstrate that water colour and acidity are associated. Both colour and acidity are produced in response to induced drought, have similar responses to rewetting, and are correlated with each other. These results are therefore consistent with earlier observations, which indicate that water is discoloured by organic acidic materials, products of peat decomposition.

Figure 5.21 Variation in throughflow pH from drought induced peat during rainfall simulation.

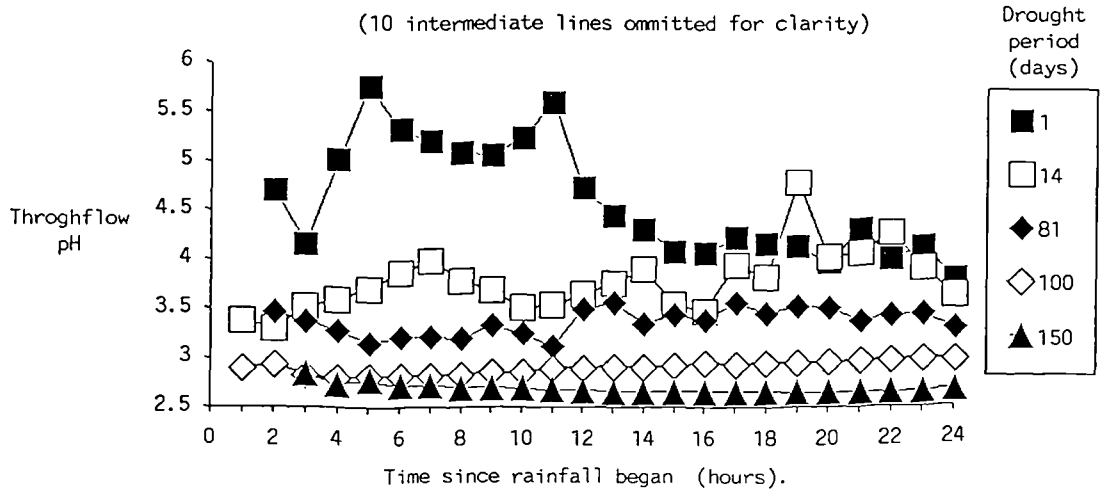
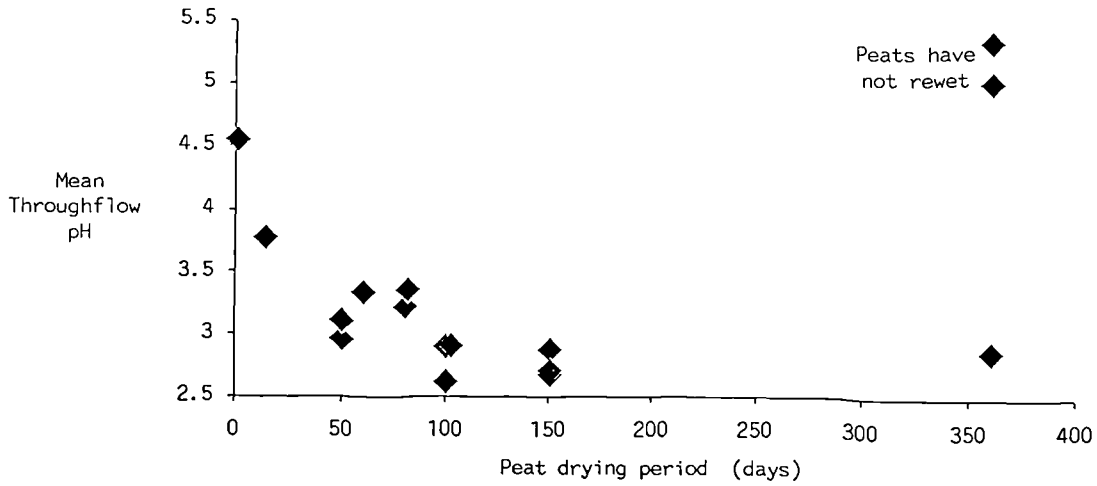


Figure 5.22 Relationship of mean throughflow pH to induced drought duration



5.9.2 Prolonged leaching with neutral and acidic rainfall

The effect of rainfall pH on colour flushed from Winter Hill peat was studied using the apparatus described in section 5.3. Three treatment groups were used; rainfall at pH 6.0 (pH6), rainfall adjusted to pH 3.0 with 0.01M sulphuric acid ($pH3_S$), and rainfall adjusted to pH 3.0 with 0.01M Hydrochloric acid ($pH3_H$). Peats were leached for thirteen days, while elute colour and volume were measured. There were ten replicates at each treatment. Eluant pH was maintained within 0.1 units of its target value.

All treatment groups exhibit the characteristic decay curve associated with the depletion of the colour store. Total colour outputs were; pH 6 51.65 au m l^{-1}, pH 3_S 33.40 au $m^{-1}l^{-1}$ and $pH3_H$ 25.99 au m l^{-1}. Rainfall at pH6 produced significantly more colour than both acidic rainfall treatments ($pH3_S$ $t=8.82$, $df=26$, $P < 0.001$; $pH3_H$ $t=10.35$, $df=28$, $P < 0.001$). This is consistent with the results presented in section 5.1, and supports the theory that colour producing materials are made less soluble by a high concentration of hydrogen ions. It is thought that Hydrogen ions bind to points on the organic acid molecules, shrinking the structure and rendering it less coloured.

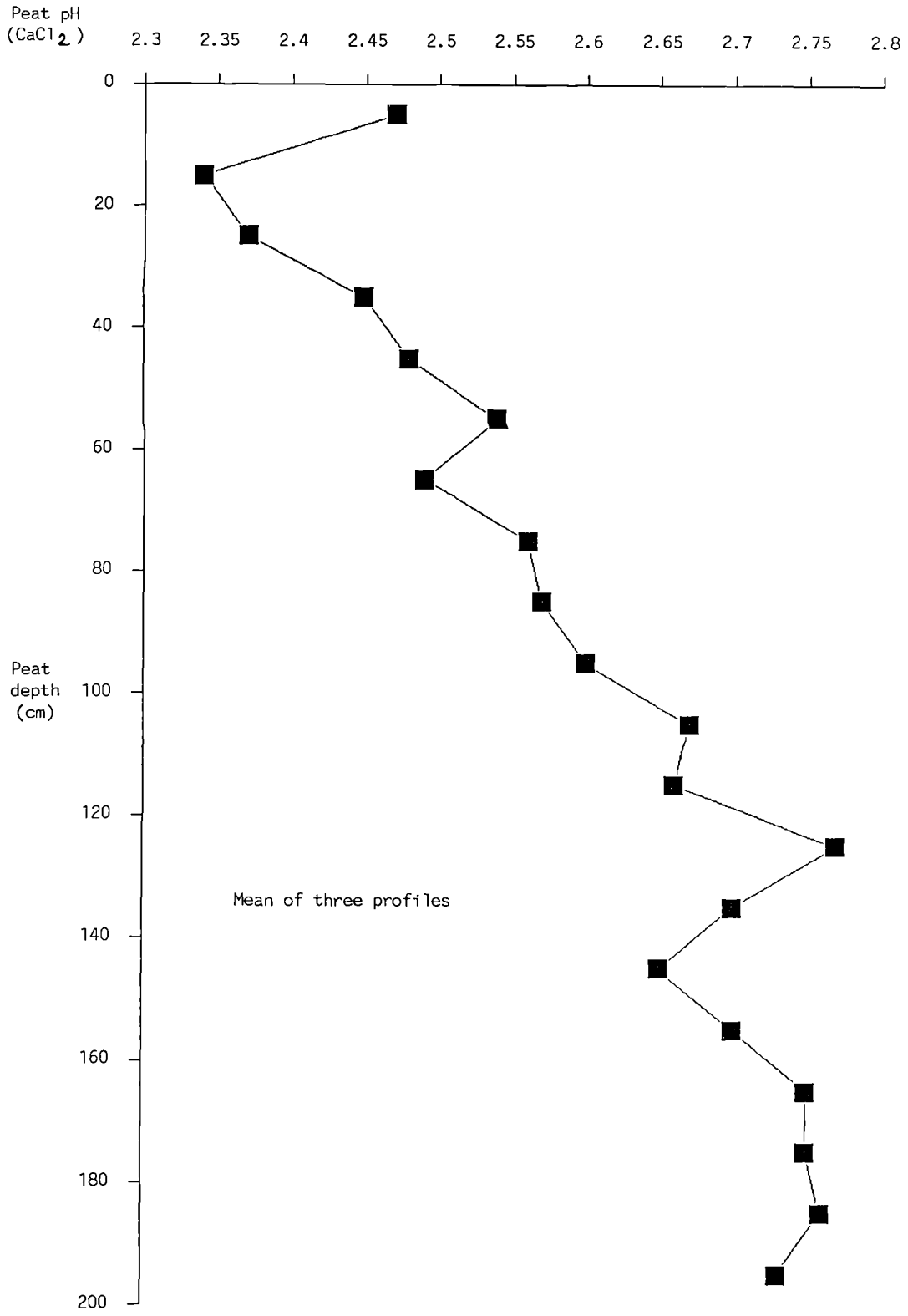
There is also a significant difference in total colour output under $pH3_S$ and $pH3_H$ rainfall ($t=2.86$, $df=26$, $P<0.01$). The greater colour output from peat leached with water adjusted to pH 3.0 using H_2SO_4 may be a consequence of elevated microbiological activity. Sulphate ions can

act as energy source for certain groups of bacteria, particularly those found in acid media such as peat. Thus the sulphate ions in $pH3_H$ rainfall may encourage bacteria driven decompositional processes, and thus increase the availability of colour producing organic matter. In the natural environment only relatively small changes in factors such as rainfall composition are likely occur. These changes may be of limited significance on direct solubilisation of colour, but may significantly affect colour availability and solubility through biological pathways.

Observations have indicated that a reduction in soil moisture is accompanied by an increase in peat acidity (figure 5.20). Soil moisture losses of ≤ 20 % (within critical moisture loss for surface peat) were associated with an increase in acidity of up to 0.5 units. It is expected that peats at the interface with mineral soil or bedrock are less acidic, due to the higher availability of buffering cations. It is therefore anticipated that a pH gradient exists in peat, with most acidic peats at the surface. Field testing to a depth of two metres at Scar House pasture demonstrates that such a gradient does exist (figure 5.23). The variability of surface pH is much greater, presumably due to variable acid production and a low buffering capacity.

This pH gradient, although relatively small, in the order of 0.5 pH units, may have an impact on discolouration. The solubility of humic material increases with solution pH.

Figure 5.23 Peat pH-profile at Scar House pasture, Upper Nidd



Therefore, rainfall and a rising water table may increase near surface soil water pH and bring more humic material into solution, colouring it. It is estimated from titrations and from the observations above that an increase in soil water pH of 0.5 units will result in an increase in water colour of 5-12 %.

It is not clear whether such small changes in peat pH directly affect the activity rates of bacteria. However, peat bacteria are acidophilous and may respond to an increase in soil water pH in order to maintain the acidity of their environment. This response is likely to take the form of increased decompositional activity and therefore colour production.

5.10 The generation and removal of colour from Winter Hill peat under controlled conditions : Conclusion

Runoff is discoloured by the products of soil organic matter decomposition. The extent of discolouration is determined by the quantity of decomposition products, their solubility in water, and their removal via a hydraulic pathway.

The generation of a store of colour producing material depends greatly upon the degree to which peat is dried. The rate of colour production is rapid in peats dried to approximately 75 % moisture (w/w). If drying continues beyond this point colour production continues, but at a slower rate. This is interpreted in terms of peat pore

structure. As drying proceeds water is initially lost from macro-pores with relatively low suction pressures. Decomposition takes place on the internal walls of these pores producing potential colour forming organics. Prolonged drought, in excess of 120 days, causes micro-pores, with much higher suction pressures to be dewatered. This increases the surface area for decomposition processes to work on, increasing the colour store. Peat within a few centimetres of ground level experiences the greatest water loss in response to drought, and effectively buffers deeper peat from severe drying. Thus most colour is produced in this near surface zone. The colour store develops only if peat dries at natural rates and temperatures. Rapid soil moisture loss by high temperature drying does not increase colour. In addition peat decomposition is also partly dependent upon soil pH, although no simple relationship exists. These observations indicate that organic decomposition cannot be described purely in terms of chemical kinetics.

Without water, decomposition products remain in situ, cannot pass into solution, and so remain immobile and will not contribute to discolouration. Once decomposition products have been accessed by water, they must pass into solution before colour is manifest. Immersion of peat in water has shown that not all potential colour immediately passes into solution and that a steady colour increase over a prolonged period is observed. This may be due, in part, to the hydrophobic nature of humic molecules, decomposition

end products. Hayes (1987) has shown that on contact with water, humic molecules swell, allowing low molecular fractions to pass into solution, causing colour. This process is slow due to the initial hydrophobic state of the organics, preventing penetration of water into the structure, and the peat ped. The pH of the water is also important in determining the degree to which water becomes coloured. When the pH of the water is low, hydrogen ions associate with negatively charged groups on the humic molecule, promoting hydrogen bonding and shrinking the molecule. This reduces colour. Conversely less acidic water produces less shrinkage and therefore more colour.

Discolouration of water is very strongly related to the extent to which a peat rewets after drying. Drying produces decomposition products that are removed once water accesses peat, rewetting it. Peat can be dried beyond its critical moisture, which depends on the degree of humification and structure. If such drying takes place, rewetting is difficult due to pore collapse and chemically induced hydrophobicity. It may take several months before water can rewet such a peat sufficiently to gain physical access to pore spaces containing decomposition products, and then for humic molecules to swell and release colour producing organics. Once a peat has completely rewet, the rate of colour removal is directly proportional to the throughflow rate. Prolonged rainfall will lead to the rewetting of droughted peats, while intense rainfall will flush colour from peats rapidly once they are saturated.

6. THE ROLE OF SOIL MICROORGANISMS IN COLOUR PRODUCTION

6.1 Aims and introduction

Earlier investigations into the spatial and temporal distribution of colour, and controlled investigations detailed in the previous chapter, have enabled much of the process by which runoff becomes discoloured to be identified. However, particular inadequacies are apparent in that part of the process that describes the generation or 'production' of colour producing material. Evidence for the operation of an additional process(es), resulting in the accumulation of potentially colour forming material, comes mostly from controlled investigations. These additional process(es) are thought to be biologically orientated.

The growth of a colour store within peat is dependent upon peat temperature and pH. However, no simple function describes the relationship between colour and these factors and suggests that chemical reaction kinetics are inadequate in accounting for colour variation. The relationship between peat temperature and colour production breaks down when temperatures of near 45°C are exceeded. This is a relatively low temperature in terms of purely chemical reaction kinetics and may demarcate the point where denaturation begins. Denaturation is the state where conditions are unfavourable for the production of enzymes by bacteria, and where those existing enzymes are unable to effectively function. For several temperatures below 45°C

maximum colour output is found when the temperature is maintained at 37°C. This is a significant value, as it is the optimum temperature for the cultivation of coliforms, a large group of bacteria. Coliform bacteria exist in peat, and may play an active part in soil decomposition.

A simple exponential function describes the relationship between solution pH and the quantity of organics passing into that solution, colouring it (Tipping, 1987). This is attributed to the availability of hydrogen binding sites. However, no simple relationship describes the colour of water drawn from peats stored at a wide range of solution pH. Colour peaks are evident at specific pH values, suggesting the operation of a further reaction superimposed on the organic solubility function. Such a reaction, if additional to organic solubility must relate to organic matter availability, and therefore organic matter breakdown. Bacteria operate most effectively in specific, narrow pH range bands. Therefore certain bacteria may increase their production of specific enzymes, contributing to accelerated organic matter breakdown. Peats flushed with water adjusted to pH 3.0 with sulphuric acid release significantly more colour than peats flushed with water adjusted to a similar pH, but with hydrochloric acid. This may be attributed to sulphate ions, which can act as an energy source for acidophillous bacteria, common in peat, and so promote organic matter breakdown.

It has been demonstrated that soil moisture deficit has a highly significant impact on the growth of a colour store.

Peat that dries naturally has a vastly greater colour store than peat oven dried to the same extent. It is suggested that high temperature oven drying results in the death of bacterial populations, and so organic matter breakdown, and the production of colour forming organics is greatly reduced. Conversely, drying at ambient temperatures is a prolonged process and may promote the growth and activity of microorganism populations.

Controlled investigations have indicated that soil microorganisms are significant in water discoloration via organic decomposition pathways. Further evidence from the literature also suggests that soil microorganisms may be significant. For example, it has been demonstrated that colour release from a moorland watershed is a seasonal process. Similar seasonal patterns have been found for the population growth of soil bacteria and fungi for a range of moorland ecosystem (eg Latter et al., 1967). The growth of these populations was attributed to pH, soil moisture content, and temperature. Soil moisture deficit is significant in colour generation. It has been shown that the rewetting of dried low moor peat results in an increase in organic matter decomposition (Waksman, 1930; Waksman and Purvis, 1932). It has also been demonstrated that the rewetting of a dried non-peat soil results in elevated organic decomposition which was attributed to a burst of bacterial activity (Birch, 1958; Birch 1959). These moisture dependent bacterial processes may make a significant contribution to colour production in Winter

Hill peat. Several authors have also demonstrated that increases in colour within distribution systems are due to the presence of soil bacteria, particularly the Arthrobacter group (Mulder, 1964; Victoreen, 1969). Wormell (1973) has demonstrated the growth and decline of iron bacterial populations, thought to be significant in the seasonal pattern of discoloration, with the rise and fall of the water table. Walsh and Mitchell (1972) have demonstrated a pH dependent succesion of iron bacteria in acid mine wastes, and that Thiobacillus ferroxidans significantly catalyses iron oxidation below pH 3.5.

The aim of this chapter is to determine, by a further series of controlled investigation, whether soil microbes are significant in the process of water discoloration. Attempts are made to determine which microbes are responsible for colour production, how much they contribute to discoloration and how they respond to moisture status in Winter Hill peat.

6.2 Temperature dependent colour extraction

The pattern of colour production in peat was determined over a wider and more continuous temperature range than previously examined. Peat was collected from Scar House pasture, Upper Nidd (SE 068 762), homogenised, and 25±0.2 g placed into one litre of distilled water. The peat-water mix was vigorously shaken to evenly distribute the peat, then stored at constant temperature (±0.5°C) for forty-eight hours. Water temperature was set prior to peat

addition. This 'wet' method was employed as extraction of colour from peats would otherwise be complicated by peat drying. However, all water was near 100 % O_2 saturation before peat addition, and so the colour extraction cannot be considered wholly anaerobic. Three replicates were used at each 2°C interval from -8°C to 46°C.

The results, illustrated in figure 6.1, show a general increase in colour with increasing solution temperature. This is broadly consistent with the pattern expected for temperature dependent chemical kinetics and indicates that colour production has a major chemical component. This temperature dependent pattern of colour production is consistent with the theory that colour is produced seasonally, with maximum production during the warm dry summer. However, there are distinct jumps or peaks in the colour function, at 16°C, 26°C, 34°C and 38°C, that are not obviously consistent with a purely chemical reaction. The optimum activity of many bacterial groups is restricted to very narrow temperature ranges, outside which activity rates are reduced. Within these temperature ranges bacterial activity, in terms of reproduction and metabolism can be very rapid. Thus these peaks may represent temperatures at which microbiological activity enhances organic matter decomposition. Thus figure 6.1 may illustrate the superimposition of a relatively weak biological function onto a strong chemical function.

The temperature dependency displayed by extract colour has

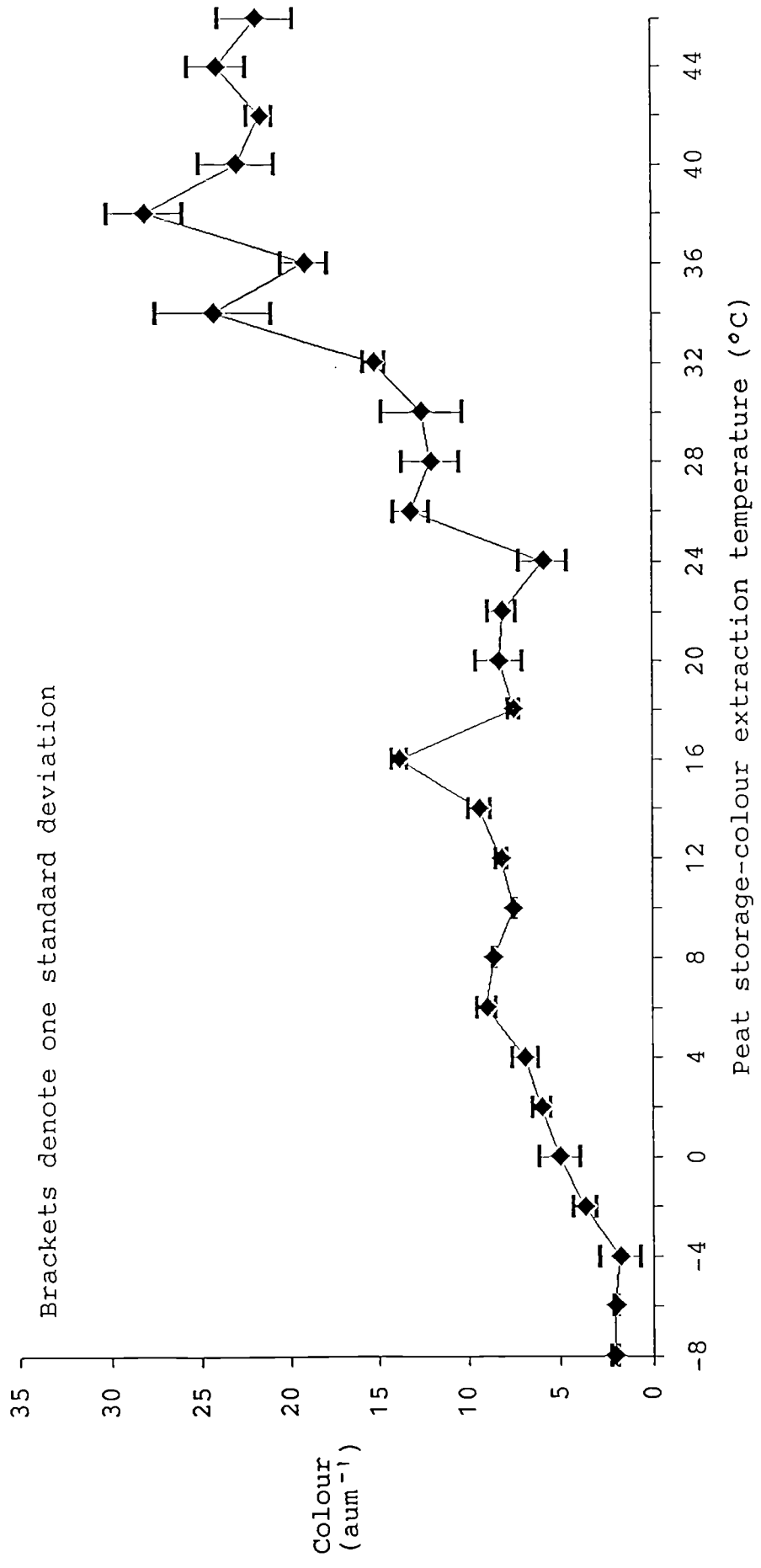


Figure 6.1 Response of peat extract colour to extraction temperature

clear implications for the seasonal pattern of colour production in upland catchments. However, small changes in temperature may produce colour increases far greater than that dictated by chemical kinetics if those temperature changes are at the point of optimum bacterial activity. Soil temperatures of 16°C may readily be achieved during summer, while temperatures of 26°C may be achieved in particularly hot years or where albedos are low, such as in areas of moorland burning or erosion. This last value is significant, as at air temperatures in excess of 25°C conditions are no longer suitable for peat accumulation. Organic matter oxidation by bacteria is rapid, and the increased activity rates result in a further elevation of temperature, and organic decomposition. This phenomena is only observed in an aerobic environment where oxidation can proceed, and is consistent with colour production in near surface peats.

6.3 Comparative microbiological activity in air dried peats

Earlier investigations demonstrated the importance of soil moisture deficit in the production of a colour store, while further investigations have suggested that the production of this store is partly dependent upon the action of soil microorganisms. In this section differences in population size of the dominant peat microorganisms, fungi and bacteria, are determined for peats from different depths, and subject to air drying at varied temperatures.

Peat samples (approximately 10 Kg each) were collected from Scar House pasture and stored at 25°C, 37°C and 44°C. After six days a sub-sample (2±0.01g) was taken from each sample and placed in 100 ml $\frac{1}{4}$-strength Ringers solution at 25°C, 37°C and 44°C, giving nine treatments. Sub-samples were taken from the centre of the initial samples, and had experienced no soil moisture loss. Peat was sampled from mean depths of 20 cm and 40 cm, giving a total of 18 treatments in all. There were three replicates for each treatment. Microbiological activity was determined after two hours and after six days of solution incubation by membrane filtration and culture on agar plates at 25°C, 37°C and 44°C. Microbiological activity was differentiated as coliforms (included all yellow, white, red and pink; number of colonies), fungal growth (usually black spore forming fungi; number of colonies) and filamentous fungi (white branched; %plate cover). No attempt was made to identify specific species. Analysis showed that all coliforms were acid, but not gas producers. Control plates had $\leq$ 2 colonies each. Results are presented in Tables 6.1-6.3.

Table 6.1. Spore forming fungi population in air dry peat

	Peat depth 20±10 cm				Peat depth 40±10 cm			
(a) Two hour incubation								
Drying	Incubation temp (°C)				Incubation temp (°C)			
Temp(°C)	25	37	44	Total	25	37	44	Total
25	14	0	0	14	4	0	0	4
37	4	0	0	4	41	0	0	41
44	24	107	22	153	353	310	276	939
Total	42	107	22	171	398	310	276	974
(b) Six day incubation								
Drying	Incubation temp (°C)				Incubation temp (°C)			
Temp(°C)	25	37	44	Total	25	37	44	Total
25	3	22	73	98	0	125	69	194
37	0	0	13	13	6	0	116	122
44	78	49	123	272	201	99	153	453
Total	81	71	209	383	207	224	338	769

Table 6.2. Filamentous fungi population in air dried peat

	Peat depth 20±10 cm				Peat depth 40±10 cm			
(a) Two hour incubation								
Drying	Incubation temp (°C)				Incubation temp (°C)			
Temp(°C)	25	37	44	Mean	25	37	44	Mean
25	25	0	23	16.0	3	0	0	1.0
37	3	0	0	1.0	0	60	55	38.3
44	7	60	90	52.3	55	90	90	58.3
Mean	11.7	20.0	37.7	23.1	19.3	50.0	48.3	39.2
(b) Six day incubation								
Drying	Incubation temp (°C)				Incubation temp (°C)			
Temp(°C)	25	37	44	Mean	25	37	44	Mean
25	0	3	40	14.3	0	40	40	26.7
37	0	0	50	16.7	2	100	55	52.3
44	0	40	25	21.7	55	90	30	58.3
Mean	0.0	14.3	38.3	17.5	19.0	76.6	41.7	45.8

Table 6.3 Coliform population in air dried peat

	Peat depth 20±10 cm				Peat depth 40±10 cm			
(a) Two hour incubation								
Drying	Incubation temp (°C)				Incubation temp (°C)			
Temp(°C)	25	37	44	Total	25	37	44	Total
25	74	18	0	92	76	30	1	107
37	116	79	0	195	21	12	0	33
44	13	0	0	13	22	2	0	24
Total	203	97	0	300	119	44	1	164
(b) Six day incubation								
Drying	Incubation temp (°C)				Incubation temp (°C)			
Temp(°C)	25	37	44	Total	25	37	44	Total
25	129	50	0	179	41	0	0	41
37	13	26	0	39	83	1	0	84
44	22	0	0	22	0	0	0	0
Total	164	76	0	240	124	1	0	125

These results demonstrate that the different groups of microbes cultured have a differential response to peat storage and solution incubation temperature. For both fungal groups growth was significantly higher in peat stored at 44°C ($t \geq 4.29$, $N=12$, $P<0.001$). Solution incubation temperature had no effect on spore forming fungi, but

increased growth of filamentous fungi at 37°C and above ($t \geq 3.00$, $N=12$, $P<0.01$). For both spore forming and filamentous fungi, growth was greater in the deeper peat samples ($t=2.673$, $N=18$, $P<0.01$; $t=3.293$, $N=18$, $P<0.01$ respectively).

Coliform growth was inversely related to peat drying temperature. Growth at 25°C was greater than at any other temperature ($t \geq 2.24$, $N=12$, $P<0.05$), while almost no cultures were observed at 44°C. A similar pattern was observed with solution incubation where growth at 25°C is greatest ($t \geq 3.32$, $N=12$, $P<0.01$). Coliform growth was almost double in the upper peat samples ($t=1.86$, $N=18$, $P<0.05$).

Although solution colour was measured, it is not related to the microbiological populations cultured, as over the temperature range studied colour is largely a product of a wet chemical, temperature dependent extraction. This would not allow the impact of microorganisms on discoloration to be isolated and assessed. These results do demonstrate that fungal populations are favoured by a relatively high temperature environment, and are more abundant in deeper peats. Conversely the coliforms favour a more moderate temperature, 25°C, and are more abundant in surface peats. Previous controlled investigations have demonstrated that colour production is greatest in surface peats, and increases rapidly near 26°C, suggesting that coliforms are the significant colour producers. However, colour production also increases with temperature, if peats are able to rewet, suggesting that fungi are also

significant, particularly during summer in sub-surface peats.

From these data no clear conclusions are drawn regarding the rôle of peat microorganisms in the discolouration of water. However, any microorganism responsible for, or making a significant contribution to colour production, may not have been enumerated using these culture techniques. Iron, sulphate reducing and acid bacteria are all possible colour producers, but have highly specific culture requirements that have not been met using the technique described here. Attempts at isolating a number of these bacteria from peats were unsuccessful (appendix III). Similarly active bacteria may have been lumped into a larger group (eg. Coliforms) and their activities masked by the presence of other less active species. Finally, activity rates may not necessarily correlate with abundance.

6.4 Colour output following microorganism control

Previous investigations have indicated that soil micro-organisms have a significant impact on discolouration. However, these investigations are inconclusive as the potential contribution of microorganisms to discolouration was complicated by additional significant factors. In this section colour output following microorganism control is investigated. Microorganisms were controlled using a variety of methods which varied in their efficacy. Once

treated, peats were flushed at a rainfall rate equivalent to 34.3mm day^{-1}, using the apparatus described in section 5.3. Microorganism activity was estimated by enumeration of coliform bacteria.

6.4.1 Wet-heat sterilisation

Microorganisms in 0.5 kg of undried peat were controlled by wet sterilisation at 120°C and 15 psi. After 48 hours coliforms in peat flushed elute were enumerated using the membrane filtration technique. Colonies were cultured on nutrient agar (appendix III) at 25°C, at 37°C and on mFc agar with rosolic acid at 37°C. Results are presented in table 6.4.

Table 6.4 Effect of wet heat peat sterilisation on colour.

(a) Culture on nutrient agar at 25°C.

	Colour (au m l^{-1})	pH	Iron (ppm)	Coliform plate count
Control	14.2	2.83	0.54	0
Wet heat	50.5	2.73	2.06	0

(b) Culture on mFc agar at 37°C.

Control	22.3	2.52	-	60
Wet heat	41.4	2.43	-	69

(c) Culture on mFc agar with Rosolic acid stain at 37°C.

Control	30.4	2.59	0.54	> 500
Wet heat	86.7	2.47	2.06	> 500

In all cases sterilisation resulted in a significant increase in colour ($t=\geq 2.62$, $N=5$, $P<0.05$). Bacterial levels were found to be similar in both control and treated peats and it is assumed this was due to initial difficulties with their enumeration. The greater colour released from sterilised peats is attributed to elevated organic matter breakdown, a result of the high temperature used in the sterilisation process. Increased colour was associated with an increase in acidity in all cases ($t\geq 3.62$, $N=5$, $P< 0.01$) which is consistent with organic matter breakdown. In those cases where iron was measured, water flushing sterilised peats was found to contain approximately four times the control concentrations ($t\geq 2.30$, $N=5$, $P< 0.05$), indicating that peat decomposition increases the availability of soluble iron.

6.4.2 Bacteria control using sodium hypochlorite

Sodium hypochlorite (sodium chlorate, $NaOCl_2$) has commonly been used to control waterborne bacteria and disinfect ground water wells in many parts of the world (Skinner and Shewan, 1978). Sodium hypochlorite (1 % v/v) was added to distilled water and used to flush 1.0 kg samples of undried Scar House peat. Total coliforms in the elute were enumerated following culture on nutrient agar at 37°C.

Figure 6.2 illustrates that the sodium hypochlorite is effective in controlling bacteria, after seven days flushing the treated group has significantly fewer coliforms ($t=4.564$, $N=5$, $P < 0.01$). However, there is also a steady increase in elute colour in the treated group, which is not apparent in the control. This colour increase is attributed to eluent pH, as discussed in chapter five, and not to reduced coliform activity. The pH effect is seen very clearly when the alkaline sodium hypochlorite is replaced with a 1 M Hcl solution, which reduces eluent pH, and results in a sharp decrease in elute colour.

6.4.3 Bacteria control with copper sulphate

Copper sulphate can act as an effective biocide if applied at the correct dose. Skinner and Shewan (op. cit.) note that regrowth of many bacterial groups in ground water wells often occurs at doses of 100 mg l^{-1} or less, but not above 1000 mg l^{-1}. Winter Hill peat was treated to control soil bacteria by adding copper sulphate to the throughflow at a dose of 250 mg l^{-1}. Results are illustrated in figure 6.3. Dosing with copper sulphate was successful in controlling bacteria (total coliforms). After two days flushing the coliform count in the treatment group was 68 % of the control, significantly lower ($t=7.938$, $N=10$, $P< 0.001$). Total coliforms in the treatment group remained significantly lower up to the thirteenth flush day ($t\geq 2.497$, $N=9$, $P < 0.05$). There was no difference in total coliform populations at thirteen days, presumably as the control population had been reduced by

Figure 6.2a Leachate colour response to bacteria control : Control group

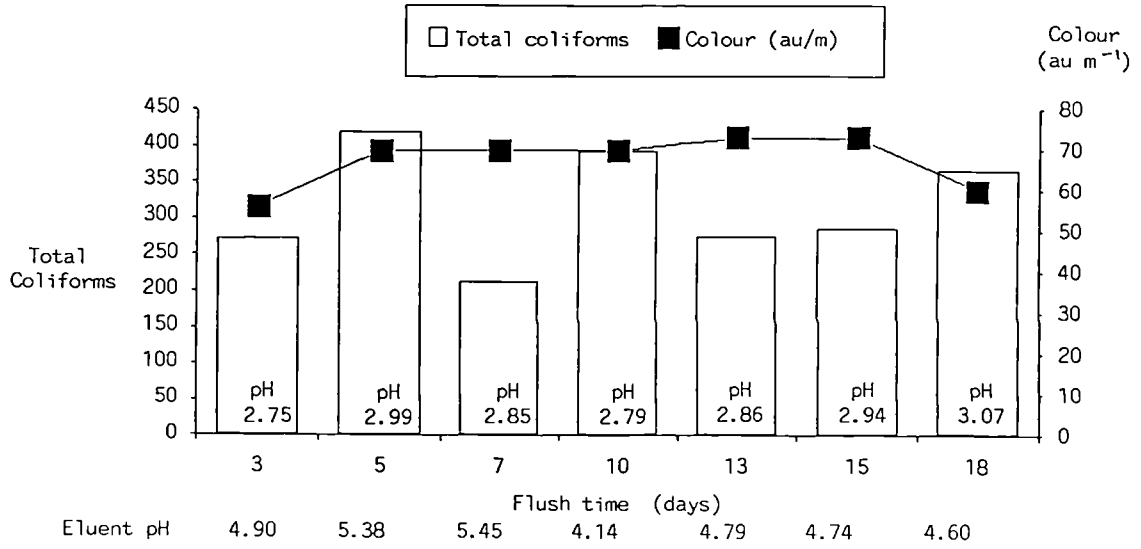


Figure 6.2b Leachate colour response to bacteria control : Treatment with sodium hypochlorite

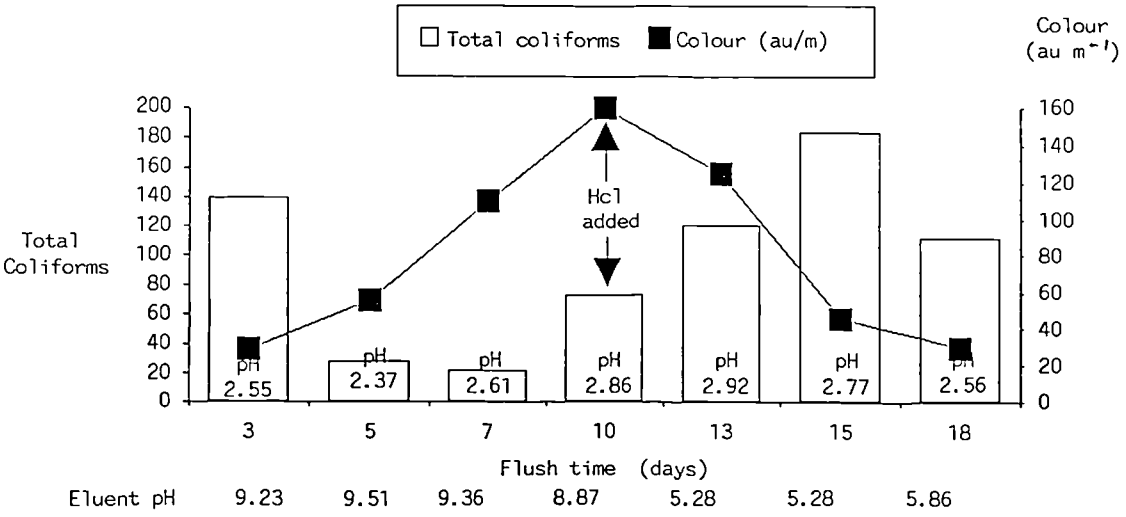


Figure 6.3a Leachate colour response to bacteria control : Control group

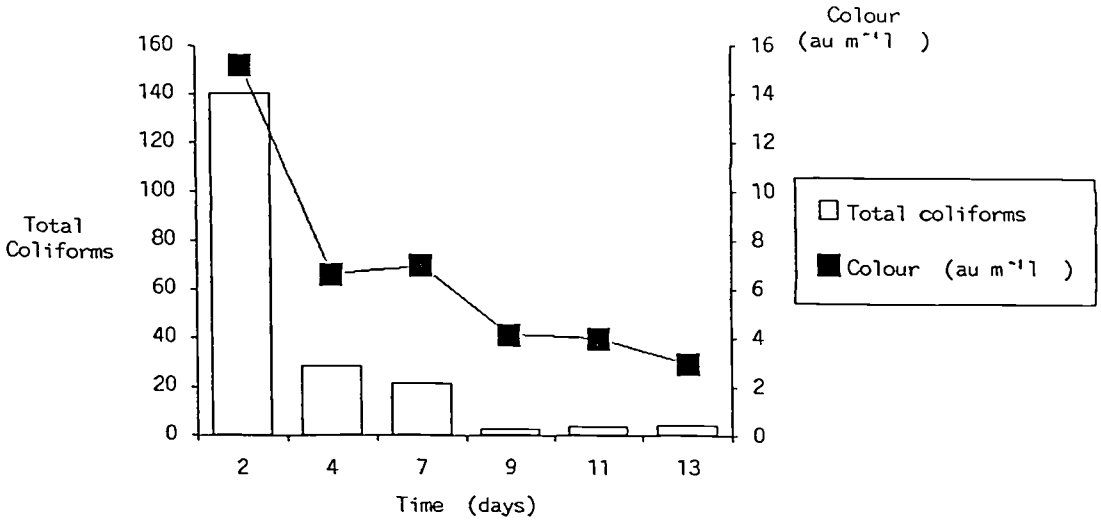
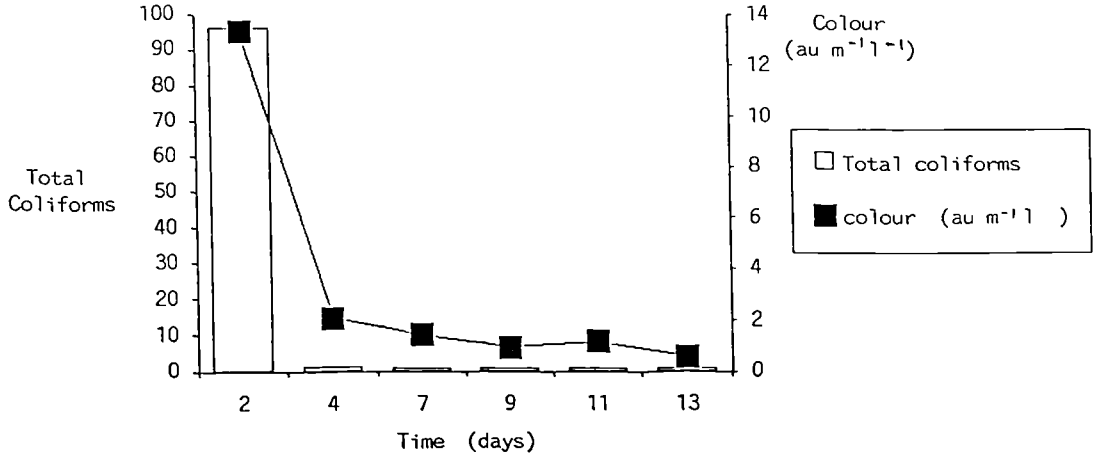


Figure 6.3b Leachate colour response to bacteria control: Treatment with 250 mg l $CuSO_4$



washout processes. After two days flushing, colour from the treatment group was 88 % of the control value, but this was not a significant difference. After four days flushing treatment colour had fallen to approximately 30 % of control values and remained so throughout the remainder of the flush period. These were significant differences ($t \geq 8.442$, $N=9$, $P < 0.001$).

It has been demonstrated that the solubility of humic substances is partly dependent upon cation status (Tipping, 1987). Therefore the possibility that adding copper sulphate reduced colour by complexation with soil organics could not be discounted. However, it was found that when a 250 mg l^{-1} copper sulphate solution was added to the control waters after flushing, a colour reduction of less than 13 % was achieved. This difference was not significant.

Copper sulphate was an effective biocide, significantly reducing the coliform population. Those coliform colonies that did grow in the treatment group were approximately $^{1}/_{10}$ th the diameter of the control colonies, indicating that stunted growth may also have added to a reduction in the total activity of the treatment population. In the absence of a viable coliform population elute colour was significantly reduced. The reduction in colour initially lagged behind the reduction in coliforms. This lag time is consistent with the cessation of colour production following a suppression of microbiological activity, and

the subsequent depletion of the existing colour store.

6.4.4 Antibiotics

Earlier control methods were successful in reducing the activity of soil microbes, estimated by total coliform abundance. However, all these methods also had some direct impact on water colour. Therefore these control methods were dropped in favour of peat dosing with an antibiotic. The antibiotic used, spectinomycin, increased eluant acidity by $\leq$ 0.1 pH units at 50 mg l^{-1}, the dose rate used, and had no other obvious unwanted side effects. All peats used were of the Winter Hill association, collected from Scar House pasture.

(a) Bacteria control in undried peat

Peat was flushed with spectinomycin dosed eluant within two hours of collection. The pattern of colour output is illustrated in figure 6.4. Total colour output from the treatment group was 67 % of the control value, and was significantly lower throughout the experimental period ($t \geq 2.929$, $N=5$, $P < 0.05$). Total coliforms were determined for the final flush day. Total coliforms in the treatment group were only 15 % of the population in the control, significantly lower ($t=9.175$, $N=50$, $P < 0.001$). These results strongly suggest that colour production is related to coliform activity.

For each of the ten peat samples flushed, mean total coliforms on the final flush day were determined from ten

Figure 6.4 Leachate colour response to bacteria control with antibiotics

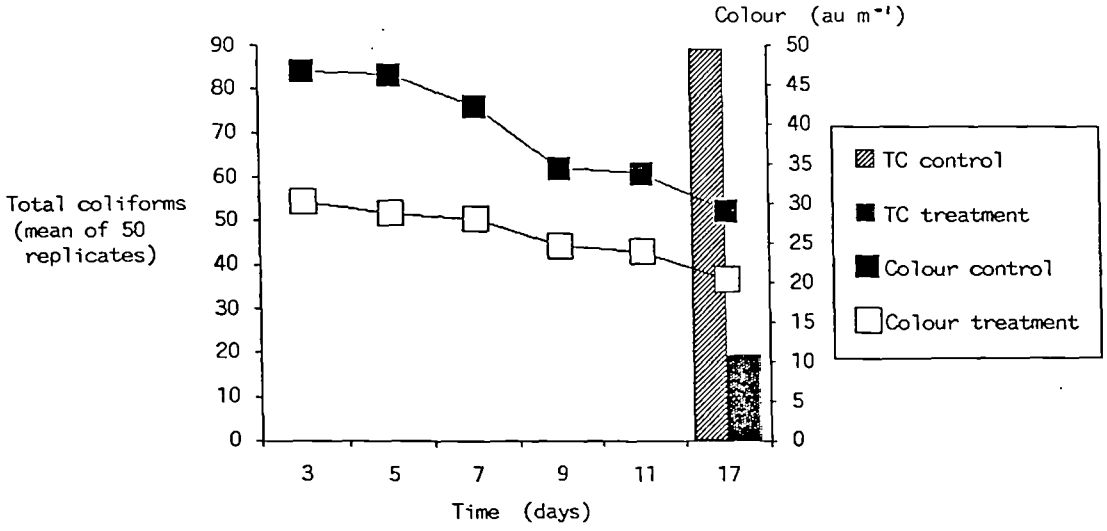
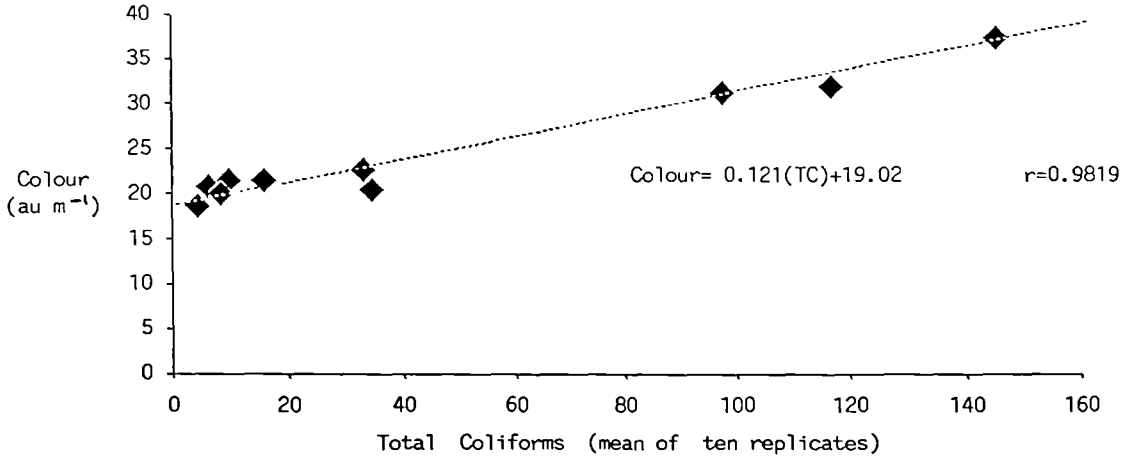


Figure 6.5 Relationship between total coliforms and leachate colour in saturated peat



replicates. A strong correlation ($r=0.9820$, $N=10$, $P< 0.001$) exists between mean total coliforms and colour. This strongly suggests that microbial activity controls colour production. Figure 6.5 shows that even with very low coliform populations peat elute is still strongly coloured. After prolonged flushing the total coliform population is depleted by washout processes. However, even if microbial activity fell to zero, chemical solubilisation and depletion of the existing store should ensure that some water discoloration continues.

(b) Bacteria control in droughted peat

Peat, stored for twelve days at 25°C, was subject to prolonged leaching with spectinomycin dosed eluant. Soil moisture deficit is known to increase colour production, therefore, the storage period was employed so as to promote the growth of any microbes contributing to colour. Compared to the undried peats discussed above, colour output was greater in both control and treatment groups. Dried control peats produced 27 % more colour ($t=12.31$, $N=25$, $P< 0.001$), while dried treatment peats produced 11 % more colour ($t=3.114$, $N=25$, $P< 0.01$). The pattern of colour output in the dried peats is illustrated in figure 6.6. Throughout the flush period, colour in the treated group was significantly less than in the control ($t\geq 4.018$, $N=5$, $P< 0.01$). Total colour output for the treatment group was 40 % of control colour. These results clearly indicate that in peat where colour production is actively proceeding, a reduction in microbial activity results in a reduction in

Figure 6.6 Leachate colour response to bacteria control with antibiotic in air dry peat

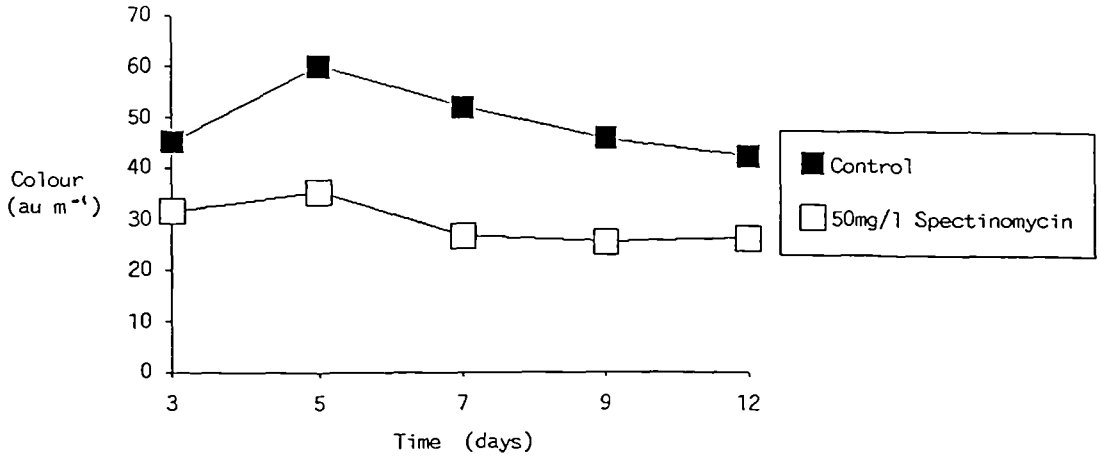
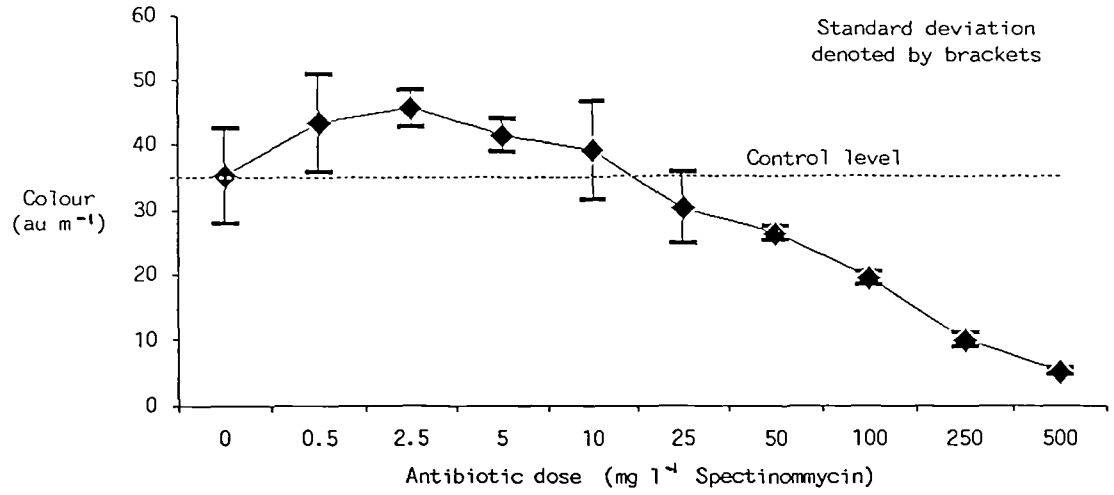


Figure 6.7 Extract colour-antibiotic dose response relationship



colour production.

(c) Serial dilution using Spectinomycin.

Previous results suggest that the size and rate of increase of the soluble colour store is closely related to past microbial activity. This observation was further tested by controlling of increase of the soluble colour store will also be low. Undried Winter Hill peat and distilled water were mixed in a ratio of 1:7 (w/v). Spectinomycin was added to the solutions in concentrations ranging from to 0 to 500 mg l^{-1}. Each mixture was gently shaken at 20°C for three days after which water colour, peat pH and total coliform determinations were made. At each dose there were three replicates. Results are illustrated in figures 6.7-6.9.

The dose response relationships displayed by extract colour and total coliforms are very similar. At doses above 10 mg l^{-1} there is a steady decline in both extract colour, and total coliforms. There is also a moderate decrease in peat pH, consistent with organic matter decomposition. At very high doses no coliforms were counted and colour was at its lowest, less than 15 % of the control value. Total coliforms were correlated with antibiotic dose ($r=-0.6437$, $N=10$, $P< 0.05$) indicating that the spectinomycin was an effective biocide. Colour was correlated with total coliforms ($r=0.8851$, $N=10$, $P< 0.001$). This strongly suggests that colour is produced by microbial activity. The possibility that total coliforms respond to colour is

Figure 6.8 Total coliform-antibiotic dose response relationship

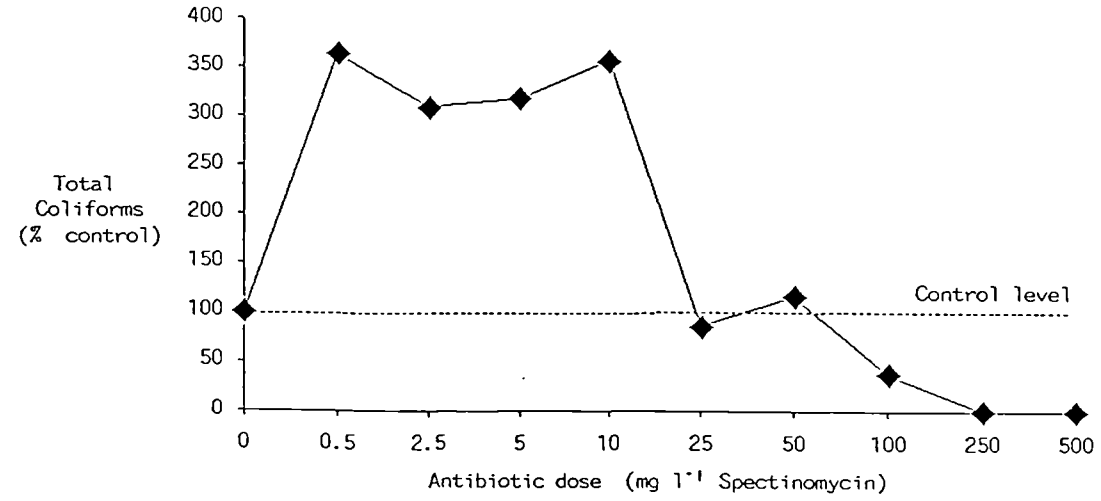
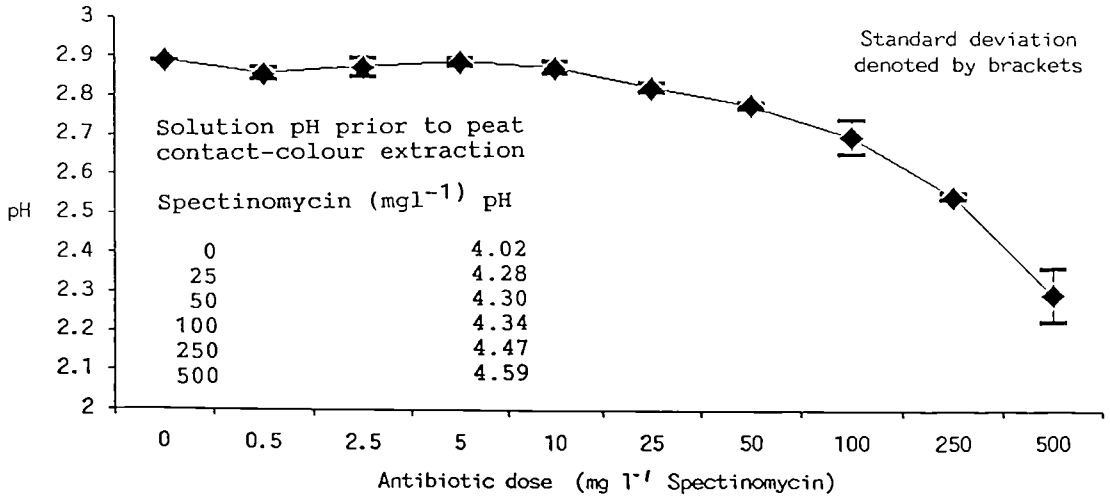


Figure 6.9 Winter Hill peat pH-antibiotic dose response relationship



discounted, as there are no obvious mechanisms which could account for a reduction in colour at high dose rates. Water-antibiotic solutions are marginally less acid at high dose rates, which from soil humic solution chemistry (Tipping, op. cit.) suggests that colour should higher, not lower.

With spectinomycin doses below 10 mg l^{-1} there are increases in both total coliform numbers and water colour in relation to their respective control values. This phenomena may be the product of mild stressing of bacteria at these low doses, resulting in increased activity. Stress responses have been observed in higher organisms including, for example, the marine mussel, Mytilus edulis (Bayne et al., 1976) and hydroids (Mitchell, 1985). Spectinomycin doses below 10 mg l^{-1} are sub-lethal and bacteria respond positively in order to ensure survival. This response may take the form of greater metabolic and reproductive rates, producing a larger population. These elevated activity rates are manifest as colour. In the natural environment a bacterial stress response may be triggered by, for example, small changes in peat pH or moisture content.

6.5 Macro respirometer studies of peat decomposition

The discolouration of runoff from upland areas arises from the solubilisation of soil organic matter. The quantity of organic matter passing into solution, colouring the soil water, depends on solution chemistry, and upon the store size of available organic matter. The size of this store is

governed by the rate at which decomposition products are removed as dissolved organic matter and the rate at which the store is replenished by further decomposition of plant material by soil micro-organisms. In this section the measurement of Winter Hill peat decomposition rates under different treatments is detailed.

6.5.1 Methodology

The rate of peat decomposition is determined by measuring the metabolic activity of peat micro-organisms. That is, their oxygen consumption or gross respiration.

(a) Description.

The macro-respirometer used in these experiments was designed by Swaby and Passey (1953) and later modified by Birch and Friend (1956). The respirometer consists of a 250 ml flask into which the peat sample is placed. A small tube containing 2 M sodium hydroxide (NaOH) absorbs the carbon dioxide evolved during microbial activity. The respirometer is kept at a constant 25°C in a water bath. The flask is made gas tight and a glass side arm taken from the flask to a bath of N. sulphuric acid. A short plastic tube is pushed onto the end of the side arm and a length of platinum wire is inserted into the tube and then bound and sealed into it. This forms the anode. The cathode, also of platinum, is sealed into a glass U-tube which is inserted into an inverted 50 ml burette. The burette is placed in the acid bath and acid is drawn up under vacuum. The burette tap is

closed when the burette is full. The electrodes are connected to 12 V DC.

(b) Operation.

As oxygen is consumed by the peat micro-organisms CO_2 is evolved and absorbed by the NaOH. This lowers the pressure in the flask and draws the H_2SO_4 up the side arm making contact with the anode. The oxygen produced at the anode diffuses back into the flask restoring atmospheric pressure, after which the contact is broken. Further respiration will close the contact. The volume of hydrogen simultaneously produced at the cathode, where its volume can be read off the burette scale, is roughly equal to twice the volume of oxygen consumed. Any imbalance between CO_2 output and oxygen consumption can be shown by determination of the respiratory quotient calculated as:

$$RQ = \frac{\text{Volume of Hydrogen produced} * 0.5}{\text{Volume of } CO_2 \text{ absorbed by NaOH}}$$

The amount of CO_2 absorbed by the NaOH is determined by titration. The 10 mls of NaOH are diluted to 100 ml at the end of the experiment. A 5 ml aliquot is titrated against 0.1 N Hcl with the end point determined by methyl orange (reading 'a'). A second 5 ml aliquot is treated with an excess of 0.4 N barium chloride solution and titrated with 0.1 N Hcl against phenolphthalien (reading 'b'). Carbon dioxide output and therefore decomposition is calculated as:

a-b * 22.4 = ml CO_2 evolved.

a-b * 12.0 = mg Carbon mineralised.

This apparatus has advantages over other respirometer set-ups. The sample is kept at normal atmospheric pressure as oxygen is automatically replaced as it is used up. The apparatus is sensitive and suitable for measuring decomposition over a period of hours to months. In addition, decomposition under anaerobic conditions can be determined by reversing the polarity of the electrodes on the battery, as the hydrogen produced by the electrolysis of the sulphuric acid is directed into the flask. For the experiments described below ten respirometer units were used. Data was not included in the analysis if the respiratory quotient was ≥ 1.5. All peat studied were of the Winter Hill association, collected from Scar House pasture, Upper Nidd.

6.5.2 Comparative decomposition rates of peat in an aerobic and anaerobic environment

The aerobic and anaerobic respiration rates of peat were determined at two moisture contents. One sample was fresh peat, with a moisture content of 86.4 %, collected 48 hours prior to being placed in the respirators. The second sample was allowed to dry naturally for four months. This sample was collected and stored in the same manner as that for peats used for artificial rainfall simulation (section 5.4). In each case respiration was determined over a fourteen day period. Results are illustrated in figure 6.10 and table 6.5.

Figure 6.10a Decomposition rates in air dry aerobic and anaerobic Winter Hill peat

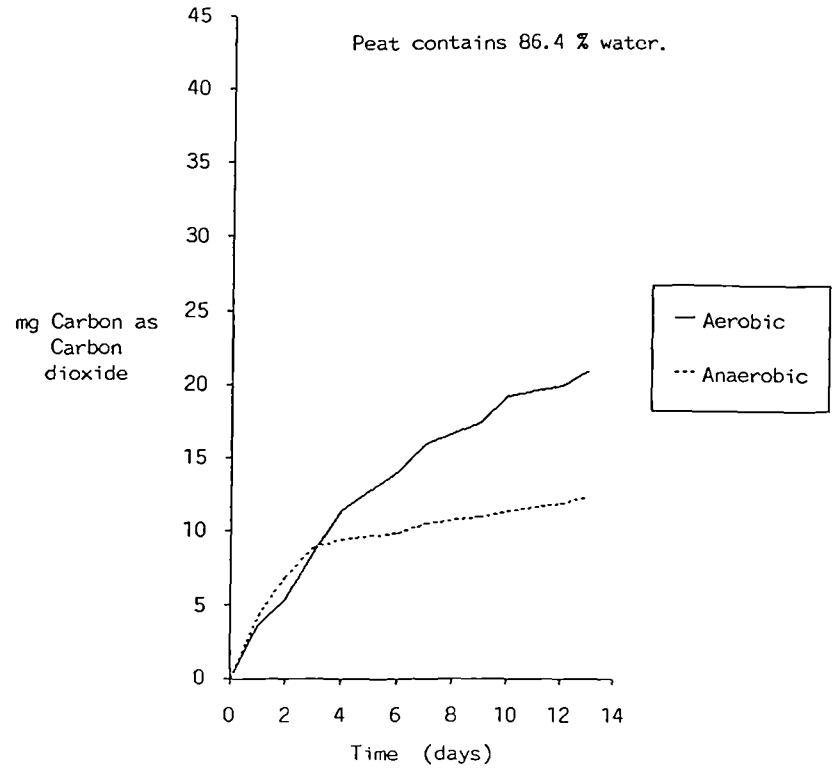


Figure6.10b Decomposition rates in air dry aerobic and anaerobic Winter Hill peat

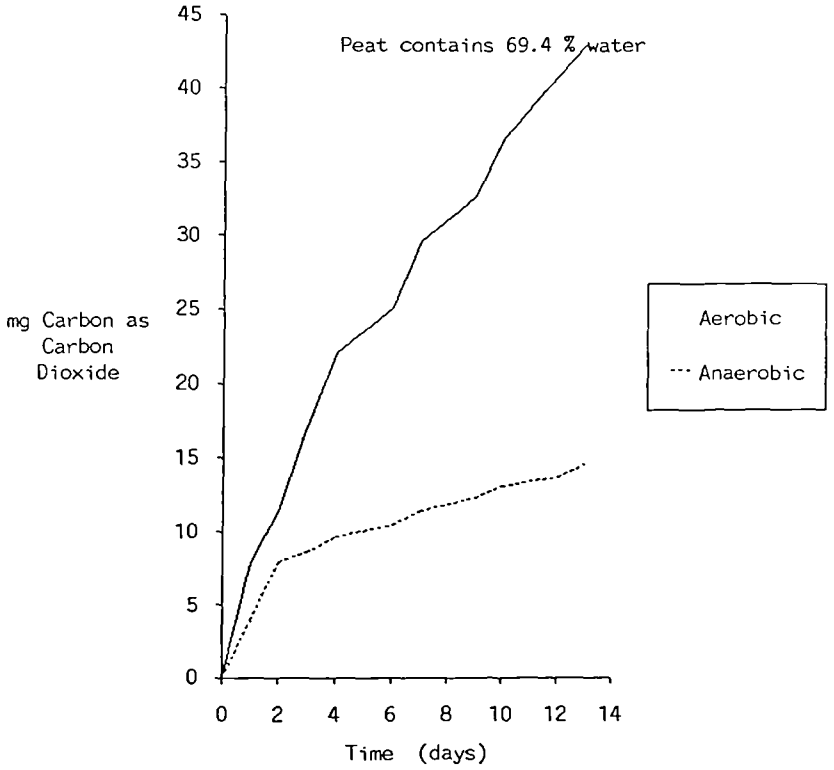


Table 6.5 Comparison of aerobic and anaerobic decomposition rates in Winter Hill peat.

(i) Peat moisture content 86.40 %

	n	RQ		$mlCO_2$		mgC		pH	
		mean	σ	mean	σ	mean	σ	mean	σ
Aerobic	4	1.03	0.10	20.72	1.86	11.1	0.99	3.43	0.30
Anaerobic	3	1.28	0.13	9.71	1.06	5.2	0.56	3.83	0.17

(ii) Peat moisture content 69.76 %

	n	RQ		$mlCO_2$		mgC		pH	
		mean	σ	mean	σ	mean	σ	mean	σ
Aerobic	4	1.25	0.19	35.26	3.98	18.9	2.14	2.90	0.86
Anaerobic	4	1.18	0.04	12.32	1.12	6.6	0.60	3.65	0.78

Aerobic decomposition exceeded anaerobic decomposition in both peat samples. For undried peat aerobic carbon mineralisation was more than double that in the anaerobic environment ($t=15.74$, $N=4$, $P< 0.001$). However, it should be noted that the RQ values are significantly different ($t=4.46$, $N=3$, $P< 0.05$). RQ values are equivalent for dried peats, where aerobic carbon mineralisation is near three times the anaerobic rate ($t=11.97$, $N=4$, $P< 0.001$). For both peats acidity, associated with coloured organic acids is greater following aerobic decomposition ($t\geq 3.53$, $N=3$, $P<0.05$).

Comparing peat samples indicates that anaerobic decomposition is 27 % greater in dried peat ($t=8.22$, $N=3$, $P< 0.001$), and perhaps of more significance for colour production, aerobic decomposition is 70 % greater in dried peat. Acidity is highest in aerobic dried peat.

6.5.3 The influence of moisture on decomposition rates

Further samples were taken from naturally dried peats and were placed in the respirators for 300 hours. Initial gravimetric moisture contents were 39.6, 67.4, 71.4 and 86.2 %. Results are presented in figure 6.11 and table 6.6. There were no significant differences in RQ values. Decomposition at the lowest and highest moisture content resulted in relatively slow decomposition. An optimum moisture content, where decomposition is at a maximum, appears to lie between these values. With peat moisture contents of 67.4 and 71.4 % decomposition is 2.5-3 times greater ($t\geq 7.97$, $N=7$, $P< 0.001$). Although derived using a different method, these results are comparable to those of Waksman and Purvis (op. cit.). They found decomposition of low moor Florida peats was at a maximum when moisture content was between 50 and 70 % moisture, and was significantly reduced when the peat was either wetter or drier than this. Birch (op. cit.) observed a seasonal pattern of decomposition in non-peat soils, and a reduction in decomposition rate following prolonged rainfall.

Figure 6.11 The influence of peat moisture content on decomposition rate

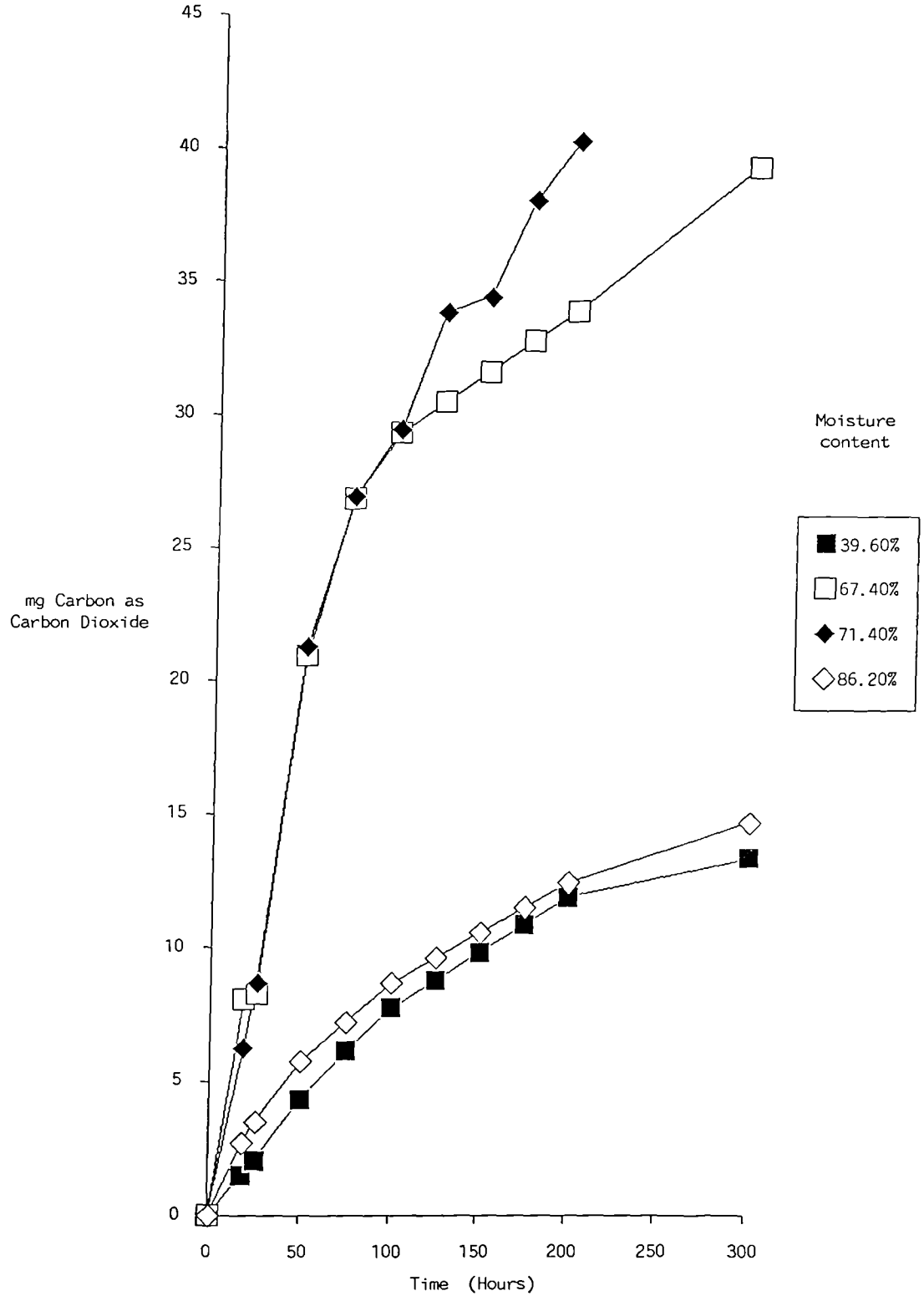


Table 6.6. The influence of moisture on the decomposition rates of Winter Hill peat.

(%) Peat moisture	n	RQ mean	RQ σ	ml CO_2 mean	ml CO_2 σ	mg C mean	mg C σ	Decompn. (% yr^{-1})*
39.6	7	1.06	0.10	6.40	1.43	3.43	0.77	0.31-0.50
67.4	8	1.03	0.04	19.04	1.12	10.32	0.60	1.12-1.26
71.4	7	1.14	0.20	18.24	3.68	9.77	1.97	1.42-2.14
86.0	7	0.98	0.10	7.68	1.11	4.11	0.59	0.41-0.55

Calculated as (365/respiration time in days)(mgC/25g)*100

The annual decomposition rates are lower than those reported by Waksman and Purvis (op. cit.), who found decomposition rates of Florida fen peats to vary from 1.6-6.6 % yr^{-1}, depending on moisture. This discrepancy may be due to the nature of the peat studied. Winter Hill peat is particularly rich in cellulose, carbohydrates and lignin, due to the high Sphagnum content, and is therefore resistant to decomposition. In addition Winter hill peats are base and nutrient poor, highly acidic and located in very wet, cold climates. Therefore annual decomposition rates may reasonably be expected to be lower than those of Florida fen peats.

6.5.4 The effect of wetting a dried peat on decomposition

An increase in decomposition rate following rewetting has been observed in both Florida fen peats (Waksman and Purvis, op.cit.) and in organic poor east African soils (Birch, op. cit). This suggests that Winter Hill peat

should also experience an increase in decomposition on rewetting. The decomposition of two Winter Hill peat groups was monitored. Both groups, treatment and control, had an initial moisture content of 67 %, after prolonged natural drying. After decomposition rates had reached a degree of stability, the treatment group was wetted to 86 % moisture, and new decomposition rates measured. Results are illustrated in figure 6.12 and table 6.7.

Table 6.7 The effect on decomposition of rewetting peat.

(a) Decomposition prior to wetting.

		RQ		$mlCO_2$		mgC	
	n	mean	σ	mean	σ	mean	σ
Control	4	0.99	0.06	20.72	2.44	11.1	1.31
Treatment	3	1.33	0.16	14.93	2.11	8.0	1.13

(b) Decomposition after raising treatment from 67-86 % moisture.

		RQ		$mlCO_2$		mgC		Extract colour (au m^{-1})	
	n	mean	σ	mean	σ	mean	σ	mean	σ
Control	4	1.05	0.09	7.46	1.06	4.00	0.56	45.00	6.90
Treatment	3	1.05	0.10	6.24	1.86	8.70	0.99	51.45	6.91

The initial peak in decomposition in both groups is

Figure 6.12 Decomposition response to rewetting in air dry peat

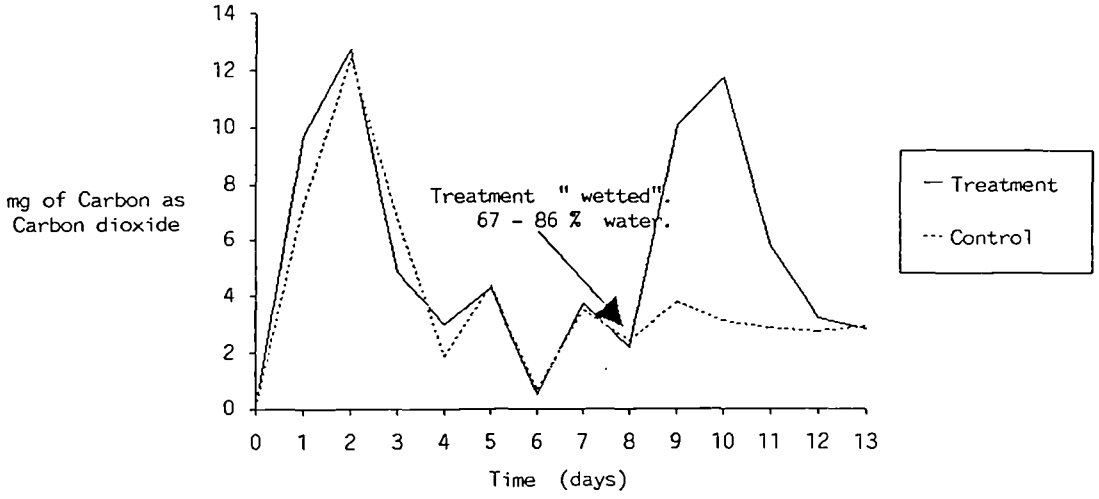
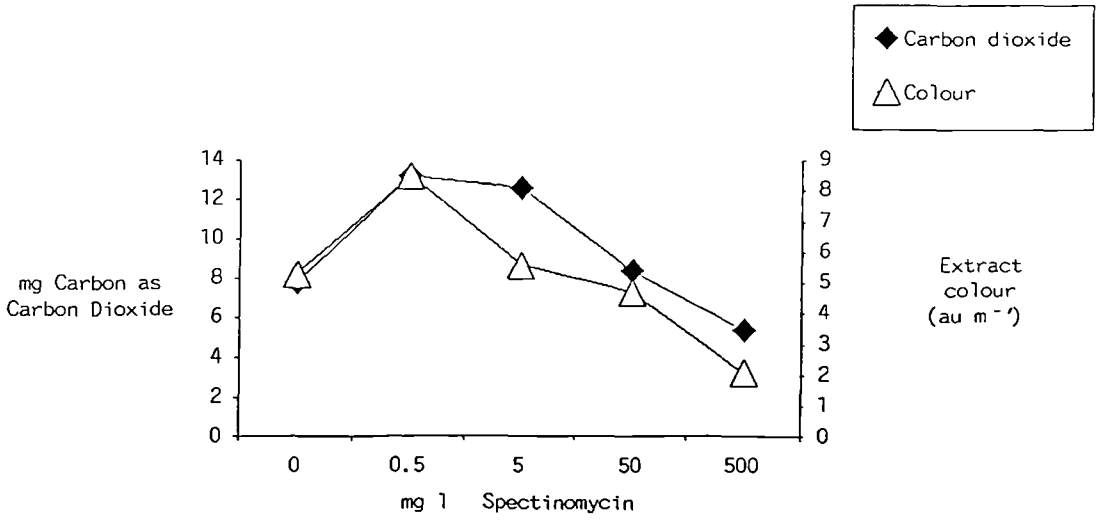


Figure 6.13 Decomposition - antibiotic dose response relationship



consistent with the initial rate of decomposition seen in figures 6.10 and 6.11. This initial rapid decomposition is believed to be a result of disturbance while the peat samples are isolated, weighed and placed in the respirometer. Disturbance brings fresh material into contact with soil bacteria responsible for decomposition processes. After four days decomposition slows, probably as the freshly exposed surfaces have little new substrate to support bacterial activity, and possibly due to the buildup of toxic microbial waste products.

Once the treatment peat is rewetted decomposition increases rapidly. Figure 6.11 suggests that increasing peat moisture content to 86 % would result in a reduction in decomposition. However, there is a clear increase in decomposition in the wetted peats ($t=9.43$, $N=3$, $P< 0.01$). This increase is thought to be a product of peat disturbance. Wetting a dry peat causes it to swell, allowing bacteria to thrive on newly exposed organic surfaces where renewed decomposition takes place. This high rate of decomposition is not sustained. Decomposition slows once the newly exposed surfaces no longer present fresh substrate to bacteria. Significantly, almost 15 % more colour was extracted under standard conditions from the wetted peats ($t=3.219$, $N=3$, $P< 0.05$).

6.5.5 The influence of Antibiotics on peat decomposition

Earlier investigations demonstrated that in the absence of an active coliform population, colour production was

significantly reduced. Serial dilution with antibiotics also suggested that colour production was increased in response to mild stressing. These observations were based on microbial activity, estimated by enumeration of total coliforms. The impact of antibiotic dose on gross respiration and extractable colour was assessed. Peat samples of standard weight were soaked in a standard volume of solution containing spectinomycin, at doses from 0-500 mg l^{-1}. Extractable colour was determined under standard conditions on completion of the respiration period. Results are presented in figure 6.13 and table 6.8.

Table 6.8. Effect of antibiotics on decomposition and colour release from Winter Hill peat.

Antibiotic dose		RQ		$mlCO_2$		mgC		Colour (au m^{-1})	
mg l^{-1}	n	mean	σ	mean	σ	mean	σ	mean	σ
0.0	2	1.11	0.03	14.56	3.36	7.8	1.8	5.3	0.6
0.5	2	1.10	0.04	24.64	4.48	13.2	2.4	8.5	0.2
5.0	2	1.12	0.02	23.52	1.12	12.6	0.6	5.6	1.1
50.0	2	1.19	0.04	15.68	0.00	8.4	0.0	4.7	0.1
500.0	2	1.28	0.16	10.08	1.12	5.4	0.6	2.1	0.0

The degree of replication does not allow levels of statistical significance to be attached to the results. However, the dose response patterns are similar to those derived previously using total coliforms as a measure of microbial activity. A high antibiotic dose results in much reduced respiration compared to the control and

correspondingly less extractable colour. In addition, at low dose rates respiration and colour were greater, possibly a product of a stress response.

6.6 Conclusion

These controlled investigations have demonstrated that a highly significant contribution is made to colour production by soil microorganisms. No specific organism was identified as being solely responsible for colour production, and it is believed that colour production is related to gross microbial metabolism. Total coliforms were associated with surface peats where colour production is greatest, while fungal groups may be significant during summer in deeper peat. A seasonal distribution in the complexation of iron and colour has previously been identified. However, the possible impact of iron oxidising and reducing bacteria could not be evaluated due to difficulties with their culture and enumeration.

The impact of soil microbes on colour was assessed by reducing microbial activity in peat and monitoring elute colour changes. In peats where total coliforms were reduced by ≥ 80 %, colour was significantly reduced by 33-70 %. In peats where active colour production was demonstrated, a marked reduction in microbial activity was coincident with a 60 % reduction in leachate colour. After prolonged peat leaching and microbial control, total coliforms were found to be highly correlated with colour (r^2=0.9643). Colour is still evident in the absence of microbial activity, but is

a product of continued chemical solubilisation processes and store depletion.

The most satisfactory method of microbial control used was an antibiotic. At very low doses, from 0.5-10 % of the ED50 value, colour production and total coliforms increased significantly. This pattern was repeated when using gross respiration as a measure of microbial activity. This suggests that microbes may respond to mild stressing by increasing gross metabolic and reproductive rates, increasing organic matter decomposition. In the natural environment such stresses may result from changes in moisture content and peat pH.

Using gross respiration as a measure of microbial activity indicates that the rate of aerobic decomposition is 2-3 times greater than anaerobic decomposition, depending on peat moisture content. At moisture contents of 40 and 86 %, rates of organic decomposition were approximately equal. However, at circa 70 % moisture decomposition was up to three times as great. It was also observed that wetting a dried peat result in a short term, but significant increase in decomposition and colour production. Wetting a dried peat produced an approximate doubling in organic decomposition over a four day period. These observations are interpreted in terms of peat pore distribution and the microbial environment. With very wet peats decomposition is anaerobic, and so relatively slow. Very dry peats have low decomposition rates as the peat shrinks and so microbes do

not have access to new substrates needed for growth. Microbial metabolism may also be lowered due to unfavourable pH conditions and the accumulation of toxic metabolic waste products. Peats with circa 70 % moisture have a structure that presents a large pore surface area, or substrate, for microbial activity. These peats remain aerobic. Rewetting a dried peat causes it to swell, presenting new organic surfaces available for microbial decomposition. These organic decomposition products discolour runoff when soluble in water.

7. CONCLUSIONS AND IMPLICATIONS

The results presented in this thesis are significant in terms of the management of potable water supplies, and to an understanding of the dynamics of discolouration. These results are briefly summarised, and their implications for catchment and catchwater management are discussed. The work also has implications regarding additional research if the understanding of discolouration dynamics is to be advanced.

7.1 Summary of conclusions

7.1.1 Character, sources and timing.

Examination of local waters demonstrates that colour has very similar physio-chemical characteristics and properties to known organic fractions such as humic and fulvic acid, and it is concluded that water is coloured by fractions of dissolved organic matter, derived from plant and soil. These coloured fractions have no unique chemical structure and cannot be defined in terms of function or structure and must be defined operationally. There is strong evidence to suggest that colour intensity in organic waters is related to the concentration of iron incorporated into the structure of the organic fraction.

Although colour is derived from non-point sources, there are great spatial differences in runoff colour. These differences are a product of catchment pedology, topography and land use. The Winter Hill soil association is rich organic peat and is the dominant source of colour. The

Belmont association, with a thin surface peat layer is also significant. Colour from these areas is elevated where shallow slopes (< 5°) promote solubilisation of organic fractions, and where high drainage densities act to lower water tables promoting rapid decomposition, and permitting a faster export of organic solutes during periods of soil moisture excess. Highest colours are derived from Winter Hill peat moorland subject to burning and artificial ditching. These practices promote discolouration through their impact on the water balance. A regression model was developed using these factors and is able to predict the magnitude and spatial distribution of coloured flows. The model requires further verification.

Coloured flows exhibit great temporal variation. The seasonal pattern is highly consistent with minimum colour during summer, maximum during autumn. Temporal colour patterns are much less consistent over periods of weeks to hours, and are produced in response to changes in the water balance. Organic decomposition proceeds rapidly during periods of soil moisture deficit, while decomposition products are flushed from catchments during periods of moisture excess. This flushing phenomena is clearly seen in the positive colour response to elevated discharge. The colour producing properties of organic decomposition products are influenced by the availability of iron. A seasonal component in colour-iron complexation is evident, and is attributed to the availability and oxidation state of iron. This is determined by water table fluctuation and

temperature dependent decomposition processes.

7.1.2 The process of discolouration.

Water is discoloured as a result of a three phase process; colour production, solubilisation and subsequent removal.

(a) Colour production.

Water is coloured by organic decomposition products. The rate of production of these decomposition products is dependent upon soil moisture status, temperature, pH, peat structure and microbiological activity. The decomposition of organic matter is accelerated by increases in soil pH and temperature, but no simple relationship exists, an indication that decomposition cannot be described purely in terms of chemical kinetics.

Decomposition is a product of microbial metabolism and, in the absence of soil bacteria colour production is greatly reduced. Colour production is maximised in a narrow acidic pH range and is limited by temperatures in excess of circa 45°C. This reflects the rates of production and activity of decomposing enzymes, such as hydrolases and desmolases, produced by soil bacteria. Microbial activity is strongly regulated by soil moisture content. In saturated peats the environment is anaerobic, and the rate of decomposition is less than half the aerobic rate. In very dry peats the decomposition rate is reduced due to the accumulation of toxic metabolic waste products and the unfavourable moisture environment itself. Thus maximum decomposition

proceeds at an optimum intermediate moisture content, near 70% (w/w).

Peat pore size distribution also has a significant impact on colour production. Models of soil aggregates indicate that decomposition only takes place in soil pores, at the interface between organic matter and air or water. The total interface area determines the amount of organic matter available for decomposition at any time. Drying of peat results in the dewatering of soil pores and promotes faster aerobic decomposition. Prolonged drying overcomes high suction moisture pressures found in smaller pores, and so greatly increases the surface area upon which aerobic decomposition processes can act. Changes in peat moisture content disturb peat aggregates, exposing new substrate upon which renewed microbial activity can take place. The rewetting of dried peat can produce a temporary doubling in decomposition, and may add significantly to total annual colour production. Mild, short term microbiological stress also produces a temporary increase in colour production. This stress response is induced by unfavourable changes in the microbial environment, including peat pH, temperature, and the accumulation of toxins.

(b) Colour solubilisation.

The action of decomposition processes produces organic fractions that have the potential to discolour water. The realisation of this potential depends upon the availability of free water and its pH, iron availability and upon the

structure of organic molecules. The solubility of humic fractions is highly dependent on hydrogen ion availability, following a second order reaction. At high pH organic fractions are readily soluble and produce intense colours. Lower molecular weight fractions are most readily soluble in acidic peat environments, and are believed responsible for the majority of observed colour. In the absence of water humic molecules shrink following polar bonding and the lower molecular weight fractions are bound on the inside. On contact with water polar bonds are broken as preferential bonds are made with hydrogen ions. This causes the molecule to swell and release the low molecular weight fractions that readily discolour water. In dry peats swelling may be very slow as the humic macromolecules are hydrophobic when shrunken, preventing the penetration of water into the structure, and the peat ped. Association with cation species generally results in a reduction in colour as polar bonding is promoted. However, it is believed that combination with iron and its oxides increases colour due to its natural yellow-brown spectral properties.

(c) Colour removal.

To produce discolouration water must access decomposition products within peat, where they pass into solution, and given sufficient hydraulic conductivity are able to drain from peat as coloured runoff. This removal process is strongly dependent upon the ability of a peat to rewet

following drying. Peat can be dried beyond its critical moisture, dependent on the degree of humification and peat structure. If such drying takes place, rewetting is inhibited due to pore collapse and chemically induced hydrophobicity. It may take several months before water can rewet such a peat sufficiently to gain physical access to pore spaces containing decomposition products, and then for humic molecules to swell and release colour producing organics. Once a peat has completely rewet, the rate of colour removal is directly proportional to the throughflow rate, and is highly associated with discharge. Prolonged rainfall will lead to the rewetting of droughted peats, while intense rainfall will flush colour from peats rapidly once they are saturated.

Discolouration is a cyclical process, dominated by a "dry" stage where decomposition products are produced, and a "wet" stage where they pass into solution, and subsequently are removed as coloured water. It is the interaction of these wet and dry phases that results in the discolouration of runoff. Frequent movement from one phase to another will result in persistent discolouration of water, but to a relatively low degree. Infrequent movement between phases will result in periods of low colour during the dry phase and exceptionally high colours during the wet phase. Infrequent movement between wet and dry phases takes place when the critical moisture loss has been exceeded. Here, the soil environment is aerobic, micro-pores are dewatered presenting a large surface area of new substrate for

microbial activity, and decomposition is near its optimum moisture content, and proceeds rapidly. The decomposition rate eventually slows but as the peat cannot readily rewet light rainfall will only act to promote bursts of decomposition, and little colour will be produced. Colour is only removed in significant amounts when the hydrophobic nature of the peat has been overcome and the soil moisture deficit eliminated. This pattern of discolouration is characteristic of infrequent water table fluctuation, and is typical of drought.

7.2 Implications for management

The results of this research have implications for the management of discoloured water in two areas; catchwater and catchment management.

Catchwaters may be operated in two ways in order to reduce discolouration. Firstly, as the spatial variation in coloured flows is highly consistent, coloured water can be discarded in a systematic manner depending on the colour flux from individual sub-catchments. Catchments with extreme colour levels can be permanently excluded, while less extreme but high colours may be excluded selectively, dependent upon colour levels and opportunity costs. Secondly, as peak discharge often precedes peak colour, lag times may be exploited by automated gating of runoff so as to retain the majority of the discharge, while discarding the colour. These management strategies are discussed further in McDonald, et.al.(1990) and are currently under

evaluation. Catchwater managers should also be aware that mixing of waters of different sources may increase mean colour. Highly coloured waters are acidic, and if mixed with less acidic low colour waters, particularly water of high alkalinity, previously insoluble humics will pass into solution increasing mean colour.

Colour may also be controlled by catchment management. High colour is promoted by soil moisture deficit, therefore artificial drainage, moorland burning and erosion are all likely to produce persistently high colours. Areas of erosion may produce particularly high colours if the original sub-surface becomes the new surface. This would subject peat with abundant micro-pores to surface wetting and drying. Drainage of plateau areas will also produce greatly elevated colour levels, perhaps persisting for several decades. Therefore the implementation of erosion control strategies, and a reduction in moorland drainage should act to control colour. Moorland burning should not be eliminated, as large uncontrolled burns are inevitable and are likely to produce more severe colour problems. Individual burns should therefore be restricted to small areas, and times of low soil moisture deficit. These management operations should be avoided in sensitive catchment areas, which can be identified and mapped using the regression model developed in chapter three.

7.3 Implications for the long term trend in colour

The seasonal cycle of water discoloration is attributed to

the accumulation of organic decomposition products during the dry summer months and their subsequent removal following periods of prolonged rainfall. This gives rise to the 'autumn flush' phenomena. Particularly high colour levels were observed following the droughts of 1976 and 1984. Following these droughts, highest colours were observed not in the autumn of the drought year, although levels were high, but in the autumn flush of the following year. This lag time is interpreted in the light of peat rewetting. A significant proportion of the summer colour store will not be accessed by the autumn flush of that year. This part of the store will be removed the following autumn when the peat fully rewets, and will be added to that summer's store, producing an exceptionally intense colour flush.

If the long term climatic trend remains relatively constant then the seasonal pattern of water discoloration is also likely to remain constant. However, the most favoured climate scenario for the UK following global warming is a shift in the timing of precipitation from spring and summer to autumn (Wigley and Jones, 1987). A scenario of drier summers and wetter autumns is likely to result in later, more intense colour flushes. In addition, if summers are not only drier but warmer too, then peat microbial activity may be promoted, increasing total decomposition and the colour store. The implications of these findings are that colour levels are unlikely to fall in the near future. Indeed, global climatic change, with dryer summers and

wetter winters in the temperate latitudes, is more likely to result in more severe colour problems still. No annual mean increase in colour may be experienced, but the magnitude of autumn flushes is likely to increase.

7.3 Implications for future research

This work points to information deficiencies in three areas where further research would improve understanding of the effects of discolouration the processes involved and aid policy making and management.

Firstly, the adverse health effects of consuming coloured potable water are poorly understood. Knowledge of the mutagenic properties of chlorinated coloured water is limited by the nature of colour producing organics which have no unique chemical structure. Assessment of possible adverse health effects requires a thorough epidemiological study.

Secondly, additional study of the process of discolouration should concentrate on the rôle of soil microbial activity. The action of acidophillous and ferrous bacteria, and the part played in decomposition and iron-colour interactions should be subject to particular attention.

Finally, further research is required to fully assess the impact of upland land use on discolouration, and the validity of the process conclusion when applied to other organic rich soils. In the light of current changes in

upland land use this research should concentrate on the impact of upland afforestation and clear felling on discolouration. From our present understanding of the colour process and the nature of coniferous forest it is estimated that discolouration following clear felling may be increased by more than two orders of magnitude when compared to similar sites not subject to afforestation.

Research in these areas lies in the diverse provinces of epidemiology, microbiology, organic chemistry, pedology and hydrology, and an interdisciplinary approach is, therefore, imperative. The results presented in this thesis are incorporated in a process based computer simulation model, currently under development and evaluation. Such a model should act as an effective tool directing further research and enabling a deeper understanding of water discolouration processes to be achieved.

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APPENDIX I. RESERVOIRS INCLUDED IN REGIONAL ANALYSIS OF COLOUR DISTRIBUTION

Agden	(SE 262 925)	Midhope	(SK 223 999)
Albert	(SE 073 256)	Oakdale upper	(SE 473 961)
Angram	(SE 116 353)	Ogden	(SE 066 306)
Barden	(SE 116 353)	Osmotherley	(SE 458 962)
Beverdyke	(SE 289 543)	Rivelin	(SK 286 869)
Blackmoorfoot	(SE 098 131)	Roundhill	(SE 151 777)
Boltby	(SE 497 869)	Royd moor	(SE 224 048)
Brownhill	(SE 117 065)	Scar House	(SE 116 353)
Codbeck	(SE 463 986)	Scargill	(SE 232 535)
Dale dike	(SD 238 912)	Settle(high)	(SD 820 635)
Digley	(SE 119 068)	Silsden	(SE 044 474)
Elsack	(SE 937 482)	Snailsden	(SE 136 040)
Embsay	(SE 001 545)	Ten acre	(SE 291 542)
Fewston	(SE 185 543)	Thornton moor	(SE 049 335)
Fixby	(SE 124 197)	Thrusscross	(SE 153 578)
Gorple l.	(SD 940 314)	Walshaw dean l.	(SD 960 330)
Gorple u.	(SD 920 314)	Walshaw dean m.	(SD 966 335)
Gorpley	(SD 912 231)	Walshaw dean u.	(SD 968 345)
Harden	(SE 153 037)	Widdop	(SD 930 330)
Holmestyes	(SE 140 057)	Windlesden lower	(SE 158 019)
Ingbirchworth	(SE 218 059)	Windlesden upper	(SE 153 013)
Langsett	(SE 217 003)	Windscar	(SE 153 026)
Leighton	(SE 160 787)	Withens clough	(SD 985 233)
March Ghyll	(SE 124 510)		

APPENDIX II. ANALYTICAL OPERATING CONDITIONS

(a) Operating conditions of ion chromatograph.

Instrument	:	Dionex 4000i with ACI and software remote control
Sample volume	:	5 ml automated injection
Injection volume	:	50 µl
Guard column	:	HPIC-AG4A
Column	:	HPIC-AS4A
Injection temperature	:	18-20°C
Eluant	:	1.8 mM Sodim Carbonate 1.7 mM Sodium Hydrogen Carbonate
Eluant flow rate	:	2.0 ml min^{-1}
Suppresor	:	Anion micromembrane (AMMS)
Regenerant	:	25 mN Sulphuric acid
Regenerant flow rate	:	3 ml min^{-1} with auto regenerant
Detection	:	Conductivity detector
Expected background	:	15-20 µS
Retention times	:	Over the elution period retention time reproducibility for standard solutions was better than ± 1% of a mean value for set conditions.

Standard solution :

Component	Concentration	Salt
Fluoride	2 ppm	NaF
Chloride	3 ppm	NaCl
Nitrate	10 ppm	$NaNO_3$
Phosphate	15 ppm	KH_2PO_4
Sulphate	20 ppm	Na_2SO_4

(b) Atomic absorbtion specification

Instrument	: Pye Unicam SP9 atomic absorbtion/ emission spectrophotometer.
Light source	: Hollow cathode lamp.
Detector	: Side window photomultiplier extended S5.
Monochromator type	: Ebert diffraction grating.
Focal length	: 174mm
Aperture	: f7.7
Grating area	: 20mm x 20mm
Lines per mm	: 1200
Blaze	: 250nm
Dispersion	: 4.7nm/mm
Limiting resolution	: 0.2nm
Wavelength accuracy	: ±1.0nm
Absorbance range	: -0.05 to 1.999 A
Damping times	: 0.1, 0.5 and 2.0 seconds
Minimum sample size	: 0.5 ml
Lamp current supply	: 1 to 20 mA
Optics	: Single beam

Instumental conditions for specific elements

	Principal line (nm)	Bandpass (nm)	Flame gas (litre min-1)	
Aluminium	309.27	0.4	nitrous oxide	5.0
			acetylene	5.0
Calcium	422.67	0.4	air	5.0
			acetylene	0.9-1.1

Iron	248.33	0.2	air	5.0
			acetylene	0.8-1.0
Magnesium	285.21	0.4	air	5.0
			acetylene	1.1
Manganese	279.48	0.2	air	5.0
			acetylene	0.8-1.0

APPENDIX III. Microbiological culture

Coliform bacteria were detected and enumerated using the membrane filter technique. This technique involves the filration of an aqueous sample through a 0.45µ filter, which is incubated on a media covered plate. Modification of the culture media allows different groups of coliform bacteria to be enumerated. Results from the membrane filter technique are now considered comparable to those obtained using the most probable number (MPN) technique. A detailed methodology can be found in Rand, M.C. et al. (1976).

Media specifications.

Total coliforms: Nutrient Agar

Lab lemco powder (Oxoid).....	1.00 g
Yeast extract.....	2.00 g
Peptone.....	5.00 g
Sodium chloride.....	5.00 g
Agar Number 3 (Oxoid).....	15.00 g
Water.....	1000 ml

Iron bacteria isolation medium.

Glucose	0.15 g
Ammonium sulphate	0.50 g
Calcium nitrate	0.01 g
Dipotassium hydrogen phosphate	0.05 g
Magnesium sulphate	0.05 g
Potassium chloride	0.05 g
Calcium carbonate	0.10 g
Agar	10.00 g
Vitamin B12	0.01 mg
Thiamine	0.40 mg
Distilled water	1000 ml

Iron oxidising medium (Thiobacillus ferooxidans)

Basal salts:

Ammonium sulphate	3.00 g
Potassium chloride	0.10 g
Dipotassium hydrogen phosphate	0.50 g
Magnesium sulphate	0.50 g
Calcium nitrate	0.01 g
Sulphuric acid 10 N	1.00 ml
Distilled water	700 ml

Energy source:

Ferrous sulphate 14.74 % solution (w/v)	300 ml

Basal salts and energy source separately sterilised and combined when cool.

Sulphur medium (Thiobacillus thiooxidans)

Sulphur	10.00 g
Potassium dihydrogen phosphate	3.00 g
Magnesium sulphate	0.50 g
Ammonium sulphate	0.30 g
Calcium chloride	0.25 g
Ferric chloride	0.02 g
Distilled water	1000 ml

1 g of sulphur added to 100 ml of medium. Sterilised for 30 min on each of three consecutive days.